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MULTICOMPONENT PACKAGE

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The following statements are taken [unedited] from the documents submitted by the applicant.

The subject matter of the present invention relates to individually-portioned packages of washing or cleaning agents containing components which are active during different washing or cleaning cycles. The problem to be solved by the present invention was to make available individually-portioned packages which release washing or cleaning agent components in a suitable manner at different times of a washing or cleaning cycle. This problem is solved by washing or cleaning agents for use in the automatic washing machine or dishwasher, which

agents comprise a component that is active during the first washing or cleaning cycle and a component that is active during a subsequent washing or cleaning cycle, with the components being packaged together in an individually-portioned package, without the need of removing the components from the individually-portioned packages prior to using the agent. In addition, a method for the production of said agents is described.

The subject matter of the present invention relates to individually-portioned packages of washing or cleaning agents containing components which are active during different washing or cleaning cycles.

Washing or cleaning agents and methods for the production thereof have long been known and have been extensively described in the prior art. Normally, washing or cleaning agents are offered to the consumer in the form of spray-dried or granulated solid products or in the form of liquid products. To meet the need of consumers for possibilities of convenient doses, products in a preportioned form, in addition to the two conventional variations mentioned, have established themselves on the market and have also been described in the prior art. Thus, one can find descriptions of washing or cleaning agents in the form of compressed molded cakes, such as tablets, blocks, briquettes, rings or similar shapes, and of portions of solid and/or liquid washing or cleaning agents individually packaged in pouches.

In the case of individually-packaged portions of washing or cleaning agent quantities that are marketed in the form of individual pouches, pouches made of a water-soluble film have become especially accepted. With these pouches, the consumer does not need to tear open the package. In this manner, it is possible to conveniently dose an individual portion that is suitable for one washing or cleaning cycle by placing the pouch directly into the washing machine or automatic dishwasher, especially into the dispensing chamber of the machine, or by throwing the pouch into a certain quantity of water, for example, in a bucket, a bowl, or in the hand wash or rinse sink. Once a certain temperature has been reached, the pouch holding the washing or cleaning agent portion dissolves without leaving a residue. In addition, many variations of washing or cleaning agents packaged in pouches made of a water-soluble film have been described in the prior art.

Thus, the older Patent Application No. DE 198 31 703 discloses an individually-portioned washing or cleaning agent preparation in a pouch made of a water-soluble film, in particular in a pouch made of (potentially acetalized) polyvinyl alcohol (PVAL) in which at least 70 wt% of the particles of the washing or cleaning agent preparation have a particle size of $>800\text{ }\mu\text{m}$.

EP-B-312 277 describes individually-portioned pouches comprising a seal that disintegrates in water when subjected to mechanical stress. This heat-sealable coating is a homo- or copolymer of polyvinylpyrrolidone.

Packages of this type make it possible to easily handle individual washing or cleaning agent portions. Preportioning facilitates the dosing of the agent, and the self-soluble packaging material ensures that a contact between the user and the potentially aggressive agent is avoided during application. These packaging materials, however, have the disadvantage that they release the total individually-portioned quantity at one specific point in time. In many applications, however, it is desirable to release certain washing or cleaning agent components at one time and other components at a different time during the washing or cleaning cycle. Thus, there was a need for individually-portioned packages which specifically release such components in a suitable manner.

Thus, a first subject matter of the present invention relates to a washing or cleaning agent for use in a machine, in particular an agent for washing dishes in an automatic dishwasher, which is characterized in that it comprises one component that is active during a first washing or cleaning cycle and one component that is active during a subsequent washing or cleaning cycle and that both components together are packaged in an individually-portioned package, without the need to remove the components from the individually-portioned package prior to using the agent.

In a preferred embodiment, the individually-portioned package is a pouch made of a substantially water-insoluble material which is sealed with a water-soluble material.

Suitable water-insoluble materials include all normally used water-insoluble packaging materials that are known to the person skilled in the art. Packaging materials to be preferred are in particular synthetics based on hydrocarbons. Especially preferred water-insoluble materials include, especially, polyethylene, polypropylene and, in this particular context, in particular, oriented polypropylene, and polymer mixtures, such as mixtures comprising the previously mentioned synthetics and polyethylene terephthalate.

In this embodiment, the components are released by dissolving the water-soluble seal. This water-soluble seal may be, for example, a water-soluble adhesive.

The individually-portioned package of the preferred embodiment may also be a pouch made of a substantially water-insoluble material which has at least one sealing seam that releases the package content at a predetermined temperature.

This water-soluble seal or the sealing seam which releases the package contents at a predetermined temperature is, for example, a water-soluble adhesive. But the sealing seam may also be formed by a meltable material, in particular a hot-melt adhesive. In this case, the release takes place above the melting temperature of this substance.

Adhesives are generally divided into physically-setting adhesives (glues, pastes, solvent-based, dispersion, plastisol and hot-melt adhesives) and chemically-setting adhesives (e.g., cyanoacrylate adhesives). The physically-setting adhesives can be solvent-free (hot-melt adhesives) or solvent-containing adhesives. They set by changing the aggregate state or by evaporating the solvent prior to or during the bonding process and generally comprise one single component. These physically-setting adhesives are adhesives preferably used in the present invention. Especially preferred is the use of water- and solvent-free adhesives which are solid at room temperature and which are applied from the melt to the parts to be bonded and which, after having been joined, physically set in the process of cooling and solidifying. They are known as hot-melt or hot-setting or thermoplastic adhesives. The raw material basis of the hot-melt adhesives includes, among other things, ethylene-ethyl acrylate copolymers, ethylene-vinyl acetate copolymers, polyamides, polyether sulfones, polyisobutene or polyvinyl butyral, which are often used in combination with natural or synthetic resins and/or paraffins or microcrystalline waxes. In addition, the following materials of natural origin can be used as adhesives according to the present invention: gelatin, blood, alginates, shellac, tragacanth, gum arabic, agar-agar, resins, balsam, gutta-percha, bitumen and waxes. But conventional adhesives based on other artificial polymers, such as polyesters and polyurethanes, can be used as well.

In a preferred embodiment, the sealing seam comprises a substance with washing or cleaning action which is selected from the conventional components of washing or cleaning agents. This substance with washing or cleaning action may itself be a meltable substance which releases the components above its melting point or it may be a water-soluble substance. But it may also be an active substance which is merely embedded in the sealing matrix and thus is released shortly prior to the other components as the sealing matrix dissolves.

Active substances that can be principally used in this context include all commonly used components used in washing or cleaning agents. Particularly worth mentioning are active substances, such as surfactants (anionic, nonionic, cationic and amphoteric surfactants), builder substances (inorganic and organic builder substances), bleaching agents (such as peroxo bleach and chlorine bleach), bleach activators, bleach stabilizers, bleach catalysts, enzymes, special polymers (for example, those with co-builder properties), anti-graying agents, dyes and odorous substances (perfumes), without, however, restricting the term to this group of substances. The individual members of the substance classes mentioned here will be explained in greater detail in the context of listing washing or cleaning agent components below. In particular, it is also possible to use polymer adhesives which comprise poly(meth)acrylate blocks and thus have co-builder properties.

In another preferred embodiment, a mounting device is disposed on the individually-portioned pouch. Such a mounting device is preferably a means that allows a detachable

attachment of the individually-portioned package inside an automatic washing or cleaning machine, in particular an automatic dishwasher, so that the empty package can be removed after the washing or cleaning cycle is completed. In particular, the mounting device ensures that the individually-portioned package, once opened, does not clog the drain filter of the machine in the course of the washing or cleaning cycle and, for example, does not adhere to the heating elements of an automatic washing machine.

It is useful if the mounting device is a means which allows a detachable attachment of the individually-portioned package to the wall of the automatic washing or cleaning machine, in particular of the automatic dishwasher. In an alternative embodiment, the mounting device is a means that allows the individually-portioned package to be suspended in the washing or cleaning machine, in particular in the automatic dishwasher. In particular, the mounting device can be designed to have a counterpiece which is permanently installed in the washing or cleaning machine, in particular the automatic dishwasher, in association with which counterpiece a detachable attachment of the individually-portioned package is made possible. In particular, the mounting device can be a hook and loop fastener, with one part of the fastener being attached to the upper surface on the inside of the washing or cleaning machine, in particular of the automatic dishwasher.

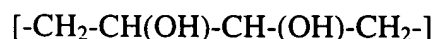
In yet another preferred embodiment of the present invention, the individually-portioned package is a pouch made of a water-soluble material, in particular a water-soluble polymer material.

Water-soluble polymer materials include principally all polymer materials that are able to completely dissolve in the aqueous phase when certain conditions are met (temperature, pH value, concentration of components with washing action). It is to be especially preferred if the polymer materials are members of groups, such as (acetalated) polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide, gelatin, cellulose, and derivatives and mixtures of the materials mentioned.

Polyvinyl alcohols (abbreviated as PVAL) are polymers of the following general structure



which comprise structural elements of the



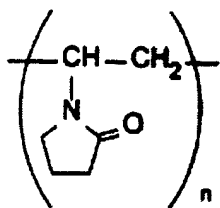
type in small quantities. Since the corresponding monomer (vinyl alcohol) is not stable in the free state, polyvinyl alcohols are obtained by way of polymer-analog reactions by means of hydrolysis, and on the industrial scale, in particular by means of an alkaline-catalyzed transesterification of polyvinyl acetates with alcohols, preferably with methanol. These industrial methods also ensure that PVALs are available which contain a predetermined residual fraction of acetate groups.

Commercially available PVALs (e.g., Mowiol® types of Hoechst) are marketed in the form of whitish-yellowish powders or granules with degrees of polymerization in the range from approximately 500 to 2500 (corresponding to relative molecular masses of approximately 20,000 to 100,000 g/mol) and have varying respective degrees of hydrolysis from 98 to 99 and from 87 to 89 mol%. Thus, these PVALs are partially saponified polyvinyl acetates with respective residual contents of acetyl groups of approximately 1 to 2 and 11 to 13 mol%.

The water solubility of PVAL can be reduced by means of a subsequent treatment with aldehydes (acetalation), by means of complexing with Ni or Cu salts, or by means of a treatment with dichromates, boric acid, or borax, thus adjusting it specifically to the values desired. Films of PVAL are largely impervious to gases, such as oxygen, nitrogen, helium, hydrogen and carbon dioxide, but they allow water vapor to penetrate.

Examples of suitable water-soluble PVAL films are the PVAL films that can be obtained under the name of "SOLUBLON®" from Syntana Handelsgesellschaft E. Harke GmbH & Co. The solubility of these PVAL films in water can be adjusted to a precise degree, and this product series offers films that are soluble in the aqueous phase in all temperature ranges relevant to the application.

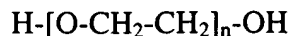
Polyvinyl pyrrolidones, known by the abbreviated name of PVP, can be described by the following general formula:



PVPs are produced by means of radical polymerization of 1-vinylpyrrolidone.

Commercially available PVPs have relative molar masses in a range from approximately 2500 to 750,000 g/mol and are offered in the form of white hygroscopic powders or as aqueous solutions.

Polyethylene oxides, abbreviated as PEOX, are polyalkylene glycols of the general formula



which are produced on an industrial scale by means of a basic-catalyzed polyaddition of ethylene oxide (oxirane) in systems which mostly contain small quantities of water, with ethylene glycol as a starter molecule. They have relative molecular masses in a range from 200 to 5,000,000 g/mol, corresponding to degrees of polymerization n of approximately 5 to >100,000. Polyethylene oxides have an extremely low concentration of reactive hydroxy end groups, and the remaining glycol properties are weak.

Gelatin is a polypeptide (relative molecular mass: approximately 15,000 to >250,000 g/mol) which is mainly obtained by hydrolysis of the collagen present in the skin and bones of animals under acid or alkaline conditions. The composition of the amino acids of the gelatins largely corresponds to that of the collagen from which it was obtained and varies depending on its provenance. Gelatin is very widely used as a water-soluble coating material, especially in the pharmaceutical industry where it is used for hard and soft gelatin capsules. Because of its high price compared to that of the polymers mentioned earlier, gelatin in the form of films is not extensively used.

Within the context of the present invention, pouches made of a water-soluble film comprising a minimum of one polymer from the groups of starches and starch derivatives, celluloses and cellulose derivatives, in particular methyl cellulose, and mixtures thereof are to be especially preferred.

Starch is a homoglycan in which the glucose units are α -glycosidically linked. Starch comprises two components of different relative molecular masses: approximately 20 to 30% of straight-chain amylose (relative molecular masses approximately 50,000 to 150,000) and 70 to 80% of branched-chain amylopectin (relative molecular masses approximately 300,000 to 2,000,000). In addition, it also contains small quantities of lipids, phosphoric acid and cations. While amylose, because of its linkage in the 1,4 position, forms long helical intertwined chains with approximately 300 to 1200 glucose molecules, the chain of amylopectin branches after an average of 25 glucose units by 1,6 linkage to a branch-like structure with approximately 1500 to 12,000 molecules of glucose. Within the context of the present invention, in addition to pure starch, starch derivatives which can be obtained by means of polymer-analogous reactions from starch are ... [word or phrase missing] ... to manufacture water-soluble enclosures for the individually-portioned washing or cleaning agents. Such chemically-modified starches include, for example, products obtained from esterifications and etherifications in which hydroxy hydrogen atoms were substituted. But starches in which the hydroxy groups have been substituted with functional groups that are not bonded via an oxygen atom can also be used as

starch derivatives. The group of starch derivatives comprises, for example, alkali starches, carboxymethyl starch (CMS), starch esters and ethers, and amino starches.

Pure cellulose has the gross molecular formula $(C_6H_{10}O_5)_n$ and is formally a β -1,4-polyacetal of cellobiose, which in turn is made up of two molecules of glucose. Suitable celluloses comprise approximately 500 to 5000 glucose units and therefore have mean relative molecular masses of 50,000 to 500,000. Disintegrating agents based on cellulose suitable for use within the context of the present invention also include cellulose derivatives which can be obtained by means of polymer-analogous reactions from cellulose. Such chemically-modified celluloses comprise, for example, products from esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. But even celluloses in which the hydroxy groups were replaced with functional groups that are not bonded via an oxygen atom can be used as cellulose derivatives. The group of cellulose derivatives includes, for example, alkali celluloses, carboxymethyl celluloses (CMC), cellulose esters and ethers, and amino celluloses.

Preferred water-soluble film pouches are made of a polymer with a relative molecular mass between 5000 and 500,000 Da, preferably between 7500 and 250,000 Da and especially between 10,000 and 100,000 Da. The water-soluble film which forms the enclosure preferably has a thickness of 1 to 150 μm , in particular of 2 to 100 μm , especially of 5 to 75 μm , and most preferably of 10 to 50 μm .

Largely regardless of whether the films are water-soluble or water-insoluble, the films can be produced using different production methods. The main methods to be mentioned are blowing, calendering and casting processes. In a preferred method, the films, starting from a melt, are blown with air over an inflating mandrel to form a tube. In the calendering method, which is also one of the preferably used production methods, the raw materials which have been plasticized by means of suitable additives are atomized through nozzles to form the films. In this case, it may be necessary to have a drying period follow the nozzle atomization. In the casting process, which is also one of the preferred production methods, an aqueous polymer preparation is applied to a heatable drying roll; after evaporation of the water, the film is optionally cooled, and subsequently the film is removed. If desired, powder can also be sprinkled on the film prior to or during the removal of the film.

According to the present invention, polyvinyl alcohol (PVAL) films are to be especially preferred for use as water-soluble pouches. Especially preferred are PVAL films that are soluble at a temperature in a range which corresponds to the temperature range of a washing or cleaning cycle in which the preparation comprising at least one component with washing action is to be used. Only by way of an example and not intending in any way to restrict it thereto, this temperature range for washing cycles refers to a temperature of approximately $\leq 25^\circ\text{C}$ for the prewashing cycle, a temperature of approximately $\leq 90^\circ\text{C}$ for the main washing cycle, and a

temperature of approximately $\leq 30^{\circ}\text{C}$ for the final washing cycle and/or a softener cycle; for cleaning and rinsing cycles, for example, the temperature range refers to a temperature of approximately $\leq 20^{\circ}\text{C}$ for the prerinsing cycle, a temperature of approximately $\leq 55^{\circ}\text{C}$ for the main rinsing cycle, and a temperature of approximately $\leq 65^{\circ}\text{C}$ for the final or clear rinsing cycle.

In an especially preferred modification, the contents of the individually-portioned pouch are molded cakes, in particular a minimum of one compressed and one uncompressed molded cake.

In particular, the component that is active during a first washing or cleaning cycle may be a component that is active during the main rinsing cycle of an automatic dishwasher, and the component that is active during a following washing or cleaning cycle may be a component that is active during the final rinse cycle of an automatic dishwasher. Alternatively, the component that is active during a first washing or cleaning cycle may be a washing or cleaning agent, in particular a molded cake of a washing or cleaning agent, and the component that is active during a following washing or cleaning cycle may be an auxiliary washing or cleaning agent, in particular a molded cake of an auxiliary washing or cleaning agent.

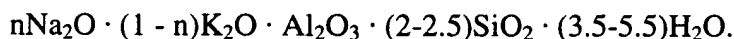
Components contained in the agents that are to be especially preferred are substances from the group of builders. In addition to components with washing action, such builders are the most important components of washing or cleaning agents. In the molded cakes of washing or cleaning agents produced according to the present invention, all builders normally incorporated into washing or cleaning agents can be used, in particular zeolites, silicates, carbonates, organic co-builders and -- unless frowned upon for ecological reasons -- phosphates. The builders mentioned can also be used in molded cakes not containing any surfactants; thus, according to the present invention, it is possible to produce molded cakes which can be used to soften water.

Suitable crystalline layered sodium silicates have the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot \text{H}_2\text{O}$, where M stands for sodium or hydrogen, x stands for a number between 1.9 and 4, and y stands for a number between 0 and 20, with the preferred value of x being 2, 3 or 4. Such crystalline layered silicates have been described, for example, in EP-A-0 164 514. Preferred crystalline layered silicates of the formula above are silicates in which M stands for sodium and x is 2 or 3. In particular, both β - and δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y\text{H}_2\text{O}$ are to be preferred, with β -sodium disilicate being obtainable by means of the method that is described in the WO A-91/08171.

Also usable are amorphous sodium silicates with a modulus of $\text{Na}_2\text{O}:\text{SiO}_2$ of 1:2 to 1:3.3, preferably of 1:2 to 1:2.8, and especially of 1:2 to 1:2.6, which dissolve with delay and which have secondary washing properties. The delay in dissolution with respect to the conventionally used amorphous sodium silicates can be obtained by means of different methods, for example, by means of a surface treatment, by compounding, compaction/compression, or by overdrying. In

the context of the present invention, the term "amorphous" is meant to include "X-ray amorphous." This means that, in X-ray diffraction experiments, the silicates do not produce any sharp X-ray reflexes, such as are typically observed for crystalline substances, but at best one or more peaks of the scattered X-ray radiation with the width of several degrees of the diffraction angle. Especially good builder properties may, however, also be obtained when the silicate particles produce smeared or even sharp diffraction peaks in electron diffraction experiments. This can be interpreted as meaning that the products have microcrystalline regions measuring 10 to several hundred nm, with values up to a maximum of 50 nm, and in particular, up to a maximum of 20 nm being preferred. Such so-called X-ray amorphous silicates which also dissolve with delay when compared to the conventional soluble glasses are described, for example, in DE-A-44 00 024. Especially preferred are compressed/compacted amorphous silicates, compounded amorphous silicates and overdried X-ray amorphous silicates.

The finely crystalline synthetic zeolite containing bound water to be used is preferably zeolite A and/or P. The zeolite P that is to be especially preferred is zeolite MAP (e.g., Doucil A24; commercial product of Crosfield). Zeolite X and mixtures of A, X and/or P, however, are also suitable for use in this context. Commercially available and preferably used within the context of the present invention is, for example, a co-crystallizate of zeolite X and zeolite A (approximately 80 wt% of zeolite X) which is distributed by CONDEA Augusta S.p.A. under the brand name of VEGOBOND AX[®], and which can be described by the following formula



The zeolite can be used both as a builder in a granular compound and for the purpose of "powdering" the entire mixture that is to be compressed, with both approaches for incorporating the zeolite into the premix being generally used. Suitable zeolites have a mean particle size of less than 10 μm (volume distribution; measuring method: Coulter counter) and preferably comprise 18 to 22 wt%, in particular 20 to 22 wt%, of bound water.

Naturally, it is also possible to use the generally known phosphates as builder substances unless such use must be avoided for ecological reasons. Particularly suitable are the sodium salts of the orthophosphates, the pyrophosphates and especially the tripolyphosphates.

Suitable organic builder substances include, for example, polycarboxylic acids which can be used in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), unless such a use is objectionable for ecological reasons, and mixtures of these. Preferred salts are the salts of polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, and mixtures of these.

Additional components that can optionally be present are alkali carriers. Alkali carriers are alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogen carbonates, alkali metal sesquicarbonates, alkali silicates, alkali metasilicates, and mixtures of the substances just mentioned, with the alkali carbonates, in particular sodium carbonate, sodium hydrogen carbonate or sodium sesquicarbonate, being preferably used within the context of the present invention.

If the agents according to the present invention are agents for use in automatic dishwashers, water-soluble builders are to be preferred since they are less likely to form insoluble residues on dishes and hard surfaces. Conventional builders -- which, in the context of the manufacture of dishwasher detergents according to the present invention, may be present in quantities between 10 and 90 wt% relative to the premix that is to be compressed -- are the low-molecular polycarboxylic acids, and their salts, the homopolymeric and copolymeric polycarboxylic acids and their salts, the carbonates, phosphates and silicates. For the production of molded cakes for use in automatic dishwashers, trisodium citrate and/or pentasodium tripolyphosphate and/or sodium carbonate and/or sodium bicarbonate and/or gluconates and/or silicate builders from the class of disilicates and/or metasilicates are preferably used. Especially, preferred is a builder system comprising a mixture of tripolyphosphate and sodium carbonate. Also especially preferred is a builder system which comprises a mixture of tripolyphosphate and sodium carbonate and sodium disilicate.

Regardless of the intended purpose, the agents usually contain builders in quantities from 20 to 80 wt%, preferably from 25 to 75 wt% and especially from 30 to 70 wt%, relative to the premix.

In addition to the builders described above, the agent can also contain substances with washing action which are important components especially for washing agents. Generally, the agents for washing textiles can contain a widely different variety of surfactants from the groups of anionic, nonionic, cationic and amphoteric surfactants, while agents for use in automatic dishwashers preferably contain only low-foaming nonionic surfactants, and water softener tablets or bleach tablets are free from surfactants.

Examples of anionic surfactants are certain types of sulfonates and sulfates. Surfactants of the sulfonate type to be used include preferably C₉-C₁₃ alkylbenzene sulfonates, olefin sulfonates, i.e., mixtures of alkene and hydroxyalkane sulfonates, and disulfonates, such as are obtained, for example, from C₁₂-C₁₈ monoolefins with terminal or internal double bonds by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acid hydrolysis of the sulfonation products. Also suitable are alkane sulfonates which are obtained from C₁₂-C₁₈ alkanes, for example, by sulfochlorination or sulfoxidation with subsequent hydrolysis and/or

neutralization. Also suitable are the esters of α -sulfo fatty acids (ester sulfonates), e.g., the α -sulfonated methyl esters of the hydrogenated coconut, palm kernel or tallow fatty acids.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters are the mono-, di- and triesters and mixtures thereof, as they are obtained in the production by means of esterifying a monoglycerol with 1 to 3 mol of fatty acid or during the transesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated fatty acids with 6 to 22 carbon atoms, for example, of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

The alk(en)yl sulfates preferred are the alkali salts, and in particular the sodium salts of the sulfuric acid semiesters of the C_{12} - C_{18} fatty alcohols, for example, coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of the C_{10} - C_{20} oxo alcohols and the semiesters of secondary alcohols with this chain length. Also preferred are alk(en)yl sulfates with the chain length mentioned which comprise a synthetic straight-chain alkyl residue that has been manufactured based on petrochemicals and which display decomposition properties similar to those of the corresponding compounds based on oleochemical raw materials. For detergent technical reasons, the C_{12} - C_{16} alkyl sulfates and C_{12} - C_{15} alkyl sulfates and the C_{14} - C_{15} sulfates are to be preferred. Other suitable anionic surfactants are 2,3-alkyl sulfates, such as are produced, for example, according to US 3,234,258 or US 5,075,041 and available as commercial products from the Shell Oil Company under the name of DAN®.

Also suitable are the sulfuric acid monoesters of the straight-chain or branched C_7 - C_{21} alcohols which have been ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl branched C_9 - C_{11} alcohols with an average of 3.5 mol of ethylene oxide (EO) or C_{12} - C_{18} fatty alcohols with 1 to 4 EO. Because of the high foaming properties, they are used only in relatively small quantities in cleaning agents, for example, in quantities of 1 to 5 wt%.

Other suitable anionic surfactants are the salts of alkyl sulfosuccinic acid which are also known as sulfosuccinates or as sulfosuccinic acid esters and which are the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols, and in particular ethoxylated fatty alcohols. Preferred sulfosuccinates comprise C_8 - C_{18} fatty alcohol residues or mixtures thereof. Especially preferred sulfosuccinates comprise a fatty alcohol residue derived from ethoxylated fatty alcohols which, when viewed separately, are nonionic surfactants (see description below). Of these, sulfosuccinates, the fatty alcohol residues of which are derived from ethoxylated fatty alcohols with a narrow homolog distribution, are to be especially preferred. Similarly, it is also possible to use alk(en)yl succinic acid with preferably 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof.

Other anionic surfactants to be taken into consideration are, in particular, soaps. Suitable are saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and especially soap mixtures derived from natural fatty acids, e.g., coconut, palm kernel or tallow fatty acids.

The anionic surfactants, including the soaps, can be used in the form of their sodium, potassium or ammonium salts and in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine. Preferably, the anionic surfactants are used in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

In the context of the present invention, washing agents are preferred which contain 5 to 50 wt%, preferably 7.5 to 40 wt%, and especially 10 to 20 wt% of anionic surfactant(s), relative to the weight of the molded cake.

As concerns the selection of anionic surfactants that are used in the washing and cleaning agents according to the present invention, there are no basic requirements with respect to the freedom of formulation that need to be met. Preferred washing agents, however, have a soap content which exceeds 0.2 wt%, relative to the overall weight. Preferably used anionic surfactants are the alkyl benzenesulfonates and fatty alcohol sulfates, with the preferred washing agents containing 2 to 20 wt%, preferably 2.5 to 15 wt%, and especially 5 to 10 wt%, of fatty alcohol sulfate(s).

The nonionic surfactants preferably used are alkoxyated, preferably ethoxylated, and especially primary alcohols with preferably 8 to 18 C atoms and an average of 1 to 12 mol of ethylene oxide (EO) per mol of alcohol, in which the alcohol residue can be linear or preferably methyl-branched in the 2-position, and linear and methyl-branched residues, such as are normally present in oxo alcohol residues, can be contained in the mixture. Especially preferred, however, are ethoxylated alcohols with residues from alcohols of natural origin having 12-18 carbon atoms, for instance, those from coconut, palm or talc, fatty alcohol or oleyl alcohol, and having an average 2-8 EO per mol alcohol. The preferred ethoxylated alcohols include, for example, C₁₂₋₁₄ alcohols with 3 EO or 4 EO, C₉₋₁₁ alcohols with 7 EO, C_{13-C15} alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C_{12-C18} alcohols with 3 EO, 5EO or 7 EO, and mixtures thereof, such as mixtures of a C_{12-C14} alcohol with 3 EO and a C_{12-C18} alcohol with 5 EO. The degrees of ethoxylation specified are statistical means which, for an individual product, may be an integral or a fractional number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols with more than 12 EO can be used as well. Examples thereof are tallow fatty alcohols with 14 EO, 25 EO, 30 EO or 40 EO.

Another class of preferably used nonionic surfactants, which are used either as the only nonionic surfactant or in combination with other nonionic surfactants, are alkoxyated, preferably

ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, preferably with 1 to 4 carbon atoms in the alkyl chain, in particular fatty acid methyl esters, such as have been described, for example, in JP 58/217598, or which are preferably manufactured according to the method described in WO A-90/13533.

Another class of nonionic surfactant that can be preferably used are the alkyl polyglycosides (APG). Alkyl polyglycosides suitable for use in this context meet the general formula $RO(G)_z$ in which R stands for a linear or branched -- in particular methyl-branched in the 2-position -- saturated or unsaturated aliphatic residues with 8 to 22, preferably 12 to 18 C atoms and in which G is the symbol denoting a glucose unit with 5 or 6 C atoms, preferably for glucose. The degree of glycosidation z is in a range between 1.0 and 4.0, preferably between 1.0 and 2.0, and especially between 1.1 and 1.4.

Preferably used are linear alkyl polyglucosides, i.e., alkyl polyglycosides, in which the polyglycosyl residue is a glucose residue and the alkyl residue is an n-alkyl residue.

The washing or cleaning agents according to the present invention can preferably contain alkyl polyglycosides, with the molded cakes preferably containing more than 0.2 wt% of APG relative to the overall molded cake. Especially preferred molded cakes of washing or cleaning agents contain APG in quantities of 0.2 to 10 wt%, preferably 0.2 to 5 wt%, and especially 0.5 to 3 wt%.

Also suitable may be nonionic surfactants of the type of amine oxides, for example, N-cocoalkyl-N,N-dimethyl amine oxide and N-tallowalkyl-N,N-dihydroxyethyl amine oxide, and the type of fatty acid alkanol amides. The quantity of these nonionic surfactants preferably measures no more than that of the ethoxylated fatty alcohols, in particular no more than half thereof.

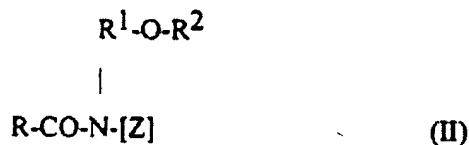
Other suitable surfactants are polyhydroxy fatty acid amides of formula (I),



in which RCO stands for an aliphatic acyl residue with 6 to 22 carbon atoms, R^1 stands for hydrogen, or an alkyl or hydroxyalkyl residue with 1 to 4 carbon atoms, and [Z] stands for a linear or branched polyhydroxyalkyl residue with 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances that can generally be obtained by means of reductive amination of a reduced sugar with ammonia, an alkylamine or an

alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of polyhydroxy fatty acid amides also includes compounds of formula (II)



in which R stands for a linear or branched alkyl or alkenyl residue with 7 to 12 carbon atoms, R^1 stands for a linear, branched or cyclic alkyl residue or an aryl residue with 2 to 8 carbon atoms, and R^2 stands for a linear, branched or cyclic alkyl residue or an aryl residue or an oxy alkyl residue with 1 to 8 carbon atoms, with $\text{C}_1\text{-C}_4$ alkyl or phenyl residues being preferred, and with [Z] standing for a linear polyhydroxyalkyl residue, the alkyl chain of which is substituted by at least two hydroxyl groups, or alkoxyated, preferably ethoxylated or propoxylated derivatives of this residue.

[Z] is preferably obtained by reductive amination of a reduced sugar, for example, glucose, fructose, maltose, galactose, mannose or xylose. For example, by following the teaching of International Patent Application No. WO A-95/07331, the N-alkoxy- or N-aryloxy-substituted compounds can subsequently be converted into the desired polyhydroxy fatty acid amides by means of a reaction with fatty acid methyl esters in the presence of an alkoxide as a catalyst.

In agents for use in dishwashers, principally all surfactants can be used as surfactant. Preferred for this particular intended purpose, however, are the nonionic surfactants described above, and in particular, the ethoxylated and/or propoxylated alcohols. To the person skilled in the art, alkoxyated alcohols are generally understood to mean the reaction products of alkylene oxide, preferably ethylene oxide, with alcohols, and within the context of the present patent, preferably the long-chain alcohols (C_{10} to C_{18} , preferably between C_{12} and C_{16} , such as C_{11} , C_{12} , C_{13} , C_{14} , C_{15} , C_{16} , C_{17} and C_{18} alcohols). As a rule, depending on the reaction conditions, n mols of ethylene oxide and one mol of alcohol will lead to a complex mixture of addition products of different degrees of ethoxylation. Another embodiment provides for the use of mixtures of alkylene oxides, preferably the mixture of ethylene oxide and propylene oxide. If desired, a subsequent etherification with short-chain alkyl groups, such as preferably the butyl group, can lead to the group of substances known as "capped" alcohol ethoxylates which can also be used in the context of the present invention. Especially preferred within the context of the present invention are the highly ethoxylated fatty alcohols or mixtures thereof with terminally capped fatty alcohol ethoxylates.

In this context, preferred are agents for use in the dishwasher which contain surfactant(s), preferably nonionic surfactant(s), in quantities of 0.5 to 10 wt%, preferably 0.75 to 7.5 wt%, and especially 1.0 to 5 wt%.

In addition to the above-described components from the group of builders and surfactants, the agent may contain other conventionally used components of washing or cleaning agents, in particular from the groups of disintegration aids, bleaches, bleach activators, enzymes, odorous substances, fluorescent agents, dyes, foam inhibitors, silicone oils, anti-redeposition agents, optical brighteners, anti-graying agents, color transfer inhibitors, corrosion inhibitors, etc.

To promote the disintegration of highly compacted molded cakes, it is possible to incorporate disintegration aids, so-called tablet disintegrants, into said molded cakes so as to shorten the disintegration time. According to Römpp (9th edition, Vol. 6, page 4440) and Voigt "Lehrbuch der pharmazeutischen Technologie" ["Manual of pharmaceutical technology"] (6th edition, 1987, pp. 182-184), tablet disintegrants or disintegration accelerators are auxiliary agents which ensure the rapid disintegration of tablets in water or gastric juice and the release of drugs in absorbable form.

These substances which, because of their action, are also called "rupturing" agents, enlarge their volume when water is added to them in that, on the one hand, their inherent volume is enlarged (swelling) and in that, through the release of gases, a pressure is generated which causes the tablets to disintegrate into smaller particles, on the other hand. Long known disintegration aids are, for example, carbonate/citric acid systems, but other organic acids may be used as well. Swelling disintegration aids include, for example, synthetic polymers, such as polyvinylpyrrolidone (PVP), or natural polymers and modified native substances, such as cellulose and starch and derivatives thereof, alginates and casein derivatives.

Preferred molded cakes of washing or cleaning agents contain 0.5 to 10 wt%, preferably 3 to 7 wt%, and especially 4 to 6 wt% of one or more disintegration aids, relative to the weight of the molded cake.

In the context of the present invention, the preferred disintegration aids used are disintegration aids based on cellulose; thus, preferred molded cakes of washing or cleaning agents contain such a disintegration aid based on cellulose in quantities of 0.5 to 10 wt%, preferably 3 to 7 wt%, and especially 4 to 6 wt%. Pure cellulose has the formal gross molecular formula $(C_6H_{10}O_5)_n$ and is formally a β -1,4-polyacetal of cellobiose, which itself has two molecules of glucose. Suitable celluloses comprise approximately 500 to 4000 glucose units and thus have mean relative molecular masses of 50,000 to 500,000. Disintegrating agents based on cellulose for use in the context of the present invention also include cellulose derivatives which can be obtained by means of polymer-analogous reactions from cellulose. Such chemically modified celluloses comprise, for example, products obtained from esterifications and

etherifications in which hydroxy hydrogen atoms were substituted. But even celluloses in which the hydroxy groups had been replaced with functional groups which are not bound via an oxygen atom can be used as cellulose derivatives. The group of cellulose derivatives includes, for example, alkali celluloses, carboxymethyl cellulose (CMC), cellulose esters and ethers, and amino celluloses. The cellulose derivatives mentioned are preferably not used as the only disintegrating agent based on cellulose, but in a mixture with cellulose. The content of cellulose derivatives in these mixtures is preferably lower than 50 wt%, especially preferred lower than 20 wt%, relative to the disintegrating agent based on cellulose. The disintegrating agent based on cellulose especially preferred is pure cellulose which is free from cellulose derivatives.

The cellulose used as a disintegration aid is preferably not used in finely dispersed form; instead, prior to adding it to the premixes to be compressed, it is converted into a coarser form, for example, it is granulated or compacted. Molded cakes of washing or cleaning agents which contain disintegrants in granular or optionally co-granular form are described in DE 197 09 991 (Stefan Herzog) and DE 197 10 254 (Henkel) and in WO 98/40463 (Henkel). These published documents also contain relatively detailed data for the production of granulated, compacted or co-granulated cellulose disintegrants. In most cases, the particle size of such disintegrating agents is higher than 200 μm , preferably at least 90 wt% have a particle size between 300 and 1600 μm , and especially at least 90 wt% have a particle size between 400 and 1200 μm . In the context of the present invention, the coarser disintegration aids based on cellulose mentioned above and described in greater detail in the documents cited are to be preferably used as disintegration aids and are commercially available from Rettenmaier, for example, under the name Arbocel® TF-30-HG.

Another disintegrating agent based on cellulose, or a constituent of this component, that can be used is microcrystalline cellulose. This microcrystalline cellulose is obtained by means of partial hydrolysis of celluloses under conditions which attack and completely dissolve only the amorphous regions (approximately 30% of the total cellulose mass) of the celluloses but leave the crystalline regions (approximately 70%) intact. A subsequent deaggregation of the microfine celluloses that are formed by hydrolysis leads to the microcrystalline celluloses which have particle sizes of approximately 5 μm and which can be compacted to form granules with a mean particle size of 200 μm .

Among the compounds that serve as bleach and produce H_2O_2 in water, sodium perborate tetrahydrate and sodium perborate monohydrate are especially important. Other useful bleaches are, for example, sodium percarbonate, peroxyphosphates, citrate perhydrates, and peracid salts or peracids that produce H_2O_2 , such as perbenzoate, peroxophthalates, diperazelaic acid or diperdodecanoic diacid. When using bleaches, it is possible to do without surfactants and/or builders, thus making it possible to prepare pure bleaching tablets. When such bleaching tablets

are to be used for washing textiles, the use of sodium percarbonate is to be preferred, regardless of any other components that may be contained in the molded cakes. When cleaning or bleaching tablets are produced for washing dishes in dishwashers, bleaching agents from the group of organic bleaching agents can be used. Typical organic bleaching agents are diacyl peroxides, such as dibenzoyl peroxide. Other typical organic bleaching agents are the peroxy acids, with the alkylperoxy acids and the arylperoxy acids being examples especially worth mentioning. Preferred members are (a) the peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but also peroxy- α -naphthoic acid and magnesium monoperphthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxy lauric acid, peroxy stearic acid, ϵ -phthalimidoperoxy caproic acid (phthalimidoperoxyhexanoic acid (PAP)), *o*-carboxybenzamidoperoxy caproic acid, *N*-nonenylamidoperadipic acid and *N*-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxydicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-diacid, and *N,N*-terephthaloyldi(6-aminopercaproic acid).

Useful bleaching agents for use in washing dishes in the dishwasher are also chlorine- and bromine-releasing substances. Among the suitable chlorine- or bromine-releasing substances, for example, heterocyclic *N*-bromo- and *N*-chloroamides, for example, trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or the salts thereof with cations, such as potassium and sodium, can be used. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethylhydantoin, can also be suitably used.

To achieve an improved bleaching effect when washing or cleaning at temperatures of 60°C and below, bleach activators can be incorporated into the premix to be compressed. Bleach activators to be used are compounds which, under perhydrolysis conditions, lead to aliphatic peroxycarboxylic acids with preferably 1 to 10 C atoms, in particular 2 to 4 C atoms, and/or optionally substituted perbenzoic acid. Suitable are substances which carry *O*- and/or *N*-acyl groups with the number of C atoms mentioned and/or optionally substituted benzoyl groups. Preferred are polyacylated alkylenediamines, in particular tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetyl glycoluril (TAGU), *N*-acylimides, in particular *N*-nonanoyl succinimide (NOSI), acylated phenol sulfonates, in particular *n*-nonanoyl- or isononanoyloxybenzene sulfonate (*n*- and iso-NOBS, respectively), carboxylic acid anhydrides, in particular phthalic acid anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

In addition to the conventional bleach activators, or instead of these, so-called bleach catalysts can be incorporated into the molded cakes. These substances are bleach-enhancing transition metal salts or transition metal complexes, such as Mn, Fe, Co, Ru or Mo salen complexes or carbonyl complexes. Also, Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands as well as Co, Fe, Cu and Ru ammine complexes can be used as bleach catalysts.

Enzymes to be used are those from the class of proteases, lipases, amylases, cellulases and mixtures thereof. Especially suitable are enzymatic active substances obtained from bacterial strains or fungi, such as *Bacillus subtilis*, *Bacillus licheniformis* and *Streptomyces griseus*. Preferably used are proteases of the subtilisin type, and in particular, proteases that are obtained from *Bacillus lentus*. Of special interest in this context are enzyme mixtures, for example, made of protease and amylase or of protease and lipase or of protease and cellulase or of cellulase and lipase or of protease, lipase and cellulase, in particular, however, cellulase-containing mixtures. Even peroxidases or oxidases have proven suitable in certain cases. The enzymes can be adsorbed to carrier substances and/or be embedded in coating substances so as to protect them against premature disintegration. The quantities of enzymes, enzyme mixtures or enzyme granules contained in the agents according to the present invention can measure, for example, 0.1 to 5 wt%, preferably 0.1 to approximately 2 wt%.

In addition, the agent may also contain components which have a positive effect on the removability of oil and grease when washing textile fabrics (so-called soil repellents). This effect is especially pronounced when a textile fabric, which had previously been washed several times with a washing agent according to the present invention which contains this oil- and grease-dissolving component, is soiled. Preferred oil- and grease-dissolving components include, for example, nonionic cellulose ethers, such as methyl cellulose and methylhydroxypropyl cellulose, with a methoxyl group content of 15 to 30 wt% and a hydroxypropoxyl group content of 1 to 15 wt% relative to the nonionic cellulose ether, and the prior-art polymers of phthalic acid and/or terephthalic acid and derivatives thereof, in particular polymers from ethylene terephthalates and/or polyethylene glycol terephthalates or anionic and/or nonionic modified derivatives thereof. Of these, the sulfonated derivatives of the phthalic acid and terephthalic acid polymers are to be especially preferred.

If the agent is a washing agent for use as a laundry detergent, it can contain derivatives of diaminostilbenedisulfonic acid or its alkali metal salts as optical brighteners. Suitable are, e.g., salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)stilbene-2,2'-disulfonic acid or similarly structured compounds which, instead of the morpholino group, contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group. In addition, brighteners of the substituted diphenyl styryl type may also be present, e.g., the

alkali salts of 4,4'-bis(2-sulfostryl) diphenyl, 4,4'-bis(4-chloro-3-sulfostryl) diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostryl) diphenyl. Mixtures of the brighteners listed above may also be used.

To improve the esthetic impression of the products being manufactured and, in addition to the softness, give the consumer a visually and sensorially pleasing "typical and unique" product, coloring and odorous substance can be incorporated into the agent. The perfume oils and odorous substances used may be certain odoriferous compounds, e.g., the synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon types. Odoriferous compounds of the ester type are, e.g., benzyl acetate, phenoxyethyl acetate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formiate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzylethyl ether, the aldehydes include, e.g., the linear alkanals with 8-18 C atoms, citral citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lillal and bourgeonal, the ketones include, e.g., α -isomethyl ionone and methyl cedryl ketone, the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol, the hydrocarbons include mainly the terpenes, such as limonene and pinene. Preferred are, however, mixtures of various odoriferous compounds which produce a pleasing odorous effect in combination with one another. Such perfume oils can also contain mixtures of natural odoriferous substances, such as are obtainable from vegetable sources, e.g., pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are nutmeg oil, sage oil, chamomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, linden oil, juniper berry oil, vetiver oil, frankincense oil, galbanum oil, labdanum oil, orange blossom oil, neroliol, orange peel oil, and sandalwood oil.

The odorous substances can be incorporated directly into the agent or into a suitable premix, but it may also be advantageous to apply the odorous substances to carriers which enhance adhesion of the perfume to the laundry and ensure a long-lasting fragrance of the fabrics by releasing the fragrance more slowly. Carrier materials that have proven especially useful are, for example, cyclodextrins; it is also possible to additionally coat the cyclodextrin-perfume complexes with other auxiliary agents.

To improve the esthetic impression of the agent, the agent (or portions thereof) can be colored with suitable dyes. Preferable dyes which can be easily selected by those skilled in the art have a high storage stability and nonreactivity with respect to the other components of the agents, as well as to light, and no pronounced substantivity on textile fibers or dishes so as to not discolor them.

If the agents are detergents for washing dishes in the dishwasher, these agents may contain corrosion inhibitors so as to protect the dishes washed or the machine, with silver-

protecting agents being especially important when dishes are washed in the dishwasher. Here, the known prior-art substances can be used. Generally, especially silver-protecting agents selected in particular from the group of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, and alkyl aminotriazoles, and their transition metal salts or complexes, can be used. Especially preferred are benzotriazole and/or alkyl aminotriazole. In addition, formulations of cleaning agents frequently are found to contain active chlorine-containing substances which are able to markedly reduce the corrosion of the surface of silver. In chlorine-free cleaners, especially oxygen and nitrogen-containing organic redox-active compounds, such as dihydric and trihydric phenols, e.g., hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucin, pyrogallol and derivatives of these classes of compounds, ... [verb missing; probably, are used]. Salt-like and complex-like inorganic compounds, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce, are often used as well. Preferred are the transition metal salts which are selected from the group of manganese and/or cobalt salts and/or complexes, especially preferred are the cobalt (ammine) complex, the cobalt (acetate) complex, the cobalt (carbonyl) complex, the chlorides of cobalt or manganese and manganese sulfate. In addition, zinc compounds to prevent corrosion of the dishes washed can be used.

According to a preferred embodiment, the agent is made available in the form of a multilayered molded cake, in particular in the form of a two-layer molded cake, in which preferably several, in particular two, different phases are present. Because of the increasing technical complexity, two-layer molded cakes are especially preferred in practice. In doing this, advantages can be obtained by incorporating certain components into the individual layers.

Preferred are, for example, agents with two different phases, with one of said phases comprising one or more bleaching agents and with the other phase comprising one or more enzymes. But advantages can be obtained not only by separating bleaching agents and enzymes; it may also be advantageous to separate bleaching agents from the bleach activators that can be optionally used so that, in addition, agents according to the present invention are preferred in which two different phases are present, with one of said phases comprising one or more bleaching agents and with the other phase comprising one or more bleaching activators.

The component that is active in the course of a following washing or cleaning cycle is preferably a molded cake of a washing or cleaning aid which comprises a coating substance.

Coating substances must be able to meet a variety of different requirements which, on the one hand, relate to the melting and solidification properties and, on the other hand, to the material properties of the coating in the solidified range at ambient temperature. Since the coating is intended to permanently protect the enclosed active substances against environmental effects during shipping or storage, it must have a high stability against impact stress occurring, for example, during packaging and shipping. Thus, the coating should either have at least

partially elastic or at least partially plastic properties so as to react to impact stress without breaking. The coating should have a melting range (solidification range) in a range of temperatures in which the active substances to be enclosed are not subjected to an excessively high thermal stress. On the other hand, however, the melting range must be sufficiently high so as to offer an effective protection to the enclosed active substances at least at a slightly increased temperature. According to the present invention, the coating substances have a melting point higher than 30°C.

It has been shown to be useful if the coating substance does not have a sharply defined melting point, as is usually the case with pure crystalline substances, but a melting range optionally comprising several degrees centigrade.

The coating substance preferably has a melting range between approximately 45°C and approximately 75°C. In the case at hand, this means that the melting range is within the temperature interval specified and does not indicate the width of the melting range. Preferably the width of the melting ranges is at least 1°C, preferably approximately 2 to approximately 3°C.

The properties mentioned above are, as a rule, implemented with the use of so-called waxes. "Waxes" are here meant to refer to a number of natural or artificial materials which, as a rule, melt above 40°C without disintegrating and which, even just barely above the melting point, have a relatively low viscosity and are not stringy. They have a highly temperature-dependent consistency and solubility.

Based on their origin, the waxes are classified into three groups, the natural waxes, chemically modified waxes and synthetic waxes.

Natural waxes include, for example, vegetable-based waxes, such as candelilla wax, carnauba wax, Japan wax, esparto grass wax, cork wax, guaruma wax, rice germ oil wax, sugar cane wax, ouricury wax or montan wax, animal waxes, such as beeswax, shellac wax, spermaceti wax, lanolin (wool wax) or uropygial grease, mineral waxes, such as ceresin or ozokerite (earth wax), or petrochemical waxes, such as petrolatum, paraffin waxes or microcrystalline waxes.

The chemically modified waxes include, for example, hard waxes, such as montan ester waxes, sasol waxes or hydrogenated jojoba waxes.

Synthetic waxes are generally understood to mean polyalkylene waxes or polyalkylene glycol waxes. Other coating materials to be used are compounds of other classes of substances which meet the softening point requirements mentioned. Synthetic compounds that were found to be suitable include, for example, higher esters of phthalic acid, in particular dicyclohexyl phthalate which is commercially available under the name Unimoll® 66 (Bayer AG). Also suitable are synthetic waxes produced from low carboxylic acids and fatty alcohols, for example, dimyristyl tartrate which is commercially available under the name Cosmacol® ETL (Condea). Conversely, it is also possible to use synthetic or partially synthetic esters of low alcohols with

fatty acids from native sources. This class of substances includes, for example, Tegin® 90 (Goldschmidt), a glycerol monostearate palmitate. According to the present invention, shellac, for example, Schellack-KPS-Dreiring-SP (Kalkhoff GmbH), can also be used as coating material.

Within the context of the present invention, the so-called wax alcohols, for example, are considered to be included among the waxes as well. Wax alcohols are higher-molecular water-insoluble fatty alcohols with generally approximately 22 to 40 carbon atoms. Wax alcohols, for example, in form of wax esters of higher-molecular fatty acids (wax acids), are the main constituent of many natural waxes. Examples of wax alcohols are lignoceryl alcohol (1-tetracosanol), cetyl alcohol, myristyl alcohol or melissyl alcohol. The coating material for the coated solid particles according to the present invention may optionally also contain wool wax alcohols, which are known as triterpenoid and steroid alcohols, for example, lanolin, which is commercially available under the trade name of Argowax® (Parmentier & Co). Other components of the coating material, of which, in the context of the present invention, at least a fraction can be used, are fatty acid glycerol esters or fatty acid alkanolamides and optionally even water-insoluble or only sparingly water-soluble polyalkylene glycol compounds.

The coating material preferably comprises paraffin wax as its main fraction. In other words, at least 50 wt% of the coating compound, preferably even more, should be made up of paraffin wax. Especially suitable are paraffin wax content in the coating material of approximately 60 wt%, approximately 70 wt%, or approximately 80 wt%, with even higher fractions of, for example, more than 90 wt% being especially preferred. In a special embodiment of the present invention, the entire coating material is made of paraffin wax.

Compared to the other natural waxes mentioned, paraffin waxes, in the context of the present invention, have the advantage that, in an alkaline cleaning agent environment, no hydrolysis of the waxes (such as is normally to be expected, for example, with wax esters) takes place since paraffin wax does not contain any hydrolizable groups.

Paraffin waxes are composed predominantly of alkanes as well as small fractions of iso- and cycloalkanes. The paraffin to be used according to the present invention preferably has no components with a melting point higher than 70°C, especially no higher than 60°C. If this melting temperature in the cleaning agent liquor falls below said temperature, fractions of alkanes with a high melting point in the paraffin can leave undesirable wax residues on the surfaces to be cleaned or on the items to be cleaned. As a rule, such wax residues lead to an unsightly appearance of the cleaned surface and should therefore be avoided. The coating material preferably contains at least one paraffin wax with a melting point of approximately 50°C to approximately 55°C.

The content of alkanes, isoalkanes and cycloalkanes that are solid at ambient temperature (generally approximately 10 to approximately 30°C) in the paraffin wax used is preferably as high as possible. The more solid wax components present in a wax at room temperature, the more useful will it be in the context of the present invention. As the content of solid wax components increases, the stress resulting from impact or friction on other surfaces that the coating material can withstand increases as well, which leads to a longer-lasting protection of the coated active substances. A high fraction of oils or liquid wax components can cause the coating material to weaken, as a result of which pores are opened and the coated active substances are exposed to the environmental effects mentioned earlier.

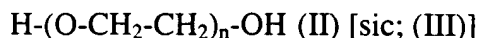
The coating material should always have the lowest possible water solubility, even in water at an increased temperature, so as to avoid a temperature-independent release of the coated active substances as much as possible.

The principle described above serves to ensure the delayed release of constituents (the active substances in the melt suspension and/or emulsion) at a specific point in time during the cleaning cycle; it can be especially well applied to automatic dishwasher detergents if rinsing in the main rinsing cycle takes place at a lower temperature (for example, 55°C) so that the active substance is released from its embedding only in the clear rinsing cycle at higher temperatures (approximately 70°C). Such an application of solidified melt suspensions has already been described in the older German Patent Applications No. 199 14 364.1 and No. 199 14 363.3.

As also described in said documents, the principle mentioned can also be reversed so that the active substance or active substances, instead of being released with delay, is/are released more rapidly. In the method according to the present invention, this can be implemented in a simple manner by using dissolution accelerators instead of dissolution-retarding agents so that the melt suspension and/or emulsion that is present in solidified form in the molded cake dose dissolves more rapidly rather than more slowly than the compressed molded cake. In contrast to the sparingly water-soluble dissolution-retarding agents described above, preferred dissolution accelerators are readily water-soluble. The water solubility of the dissolution accelerators can be markedly further increased by certain additives, for example, by incorporation of readily soluble salts or effervescent systems. Such dissolution-accelerating coating materials (with or without the addition of other dissolution-improving agents) lead to a rapid release of the coated active substances at the beginning of the cleaning cycle.

Suitable dissolution accelerators, i.e., coating materials for the accelerated release of the active substance from the core embedded in the molded cake, are in particular the previously mentioned synthetic waxes from the group of polyethylene glycols and polypropylene glycols.

Polyethylene glycols (abbreviated as PEG) that can be used according to the present invention are polymers of ethylene glycol which meet general formula III

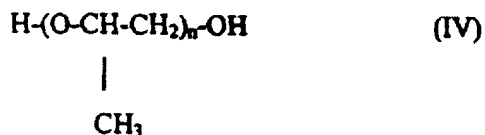


in which n can assume values between 1 (ethylene glycol) and more than 100,000. The decisive factor in an evaluation of whether or not a polyethylene glycol can be used as intended in the present invention is aggregate state of the PEG, i.e., the melting point of the PEG must be higher than 30°C, which means that the monomer (ethylene glycol) and the lower oligomers with $n = 2$ to approximately 16 cannot be used, since they have a melting point lower than 30°C. The polyethylene glycols with higher relative molecular masses are polymolecular, i.e., they are composed of collectives of macromolecules with different relative molecular masses. To identify polyethylene glycols, various nomenclatures are used which can lead to confusion. In industrial practice, the mean relative molecular mass follows "PEG," thus "PEG 200" characterizes a polyethylene glycol with a relative molecular mass of approximately 190 to approximately 210. Thus, using this nomenclature, the industrially used polyethylene glycol PEG 1550, PEG 3000, PEG 4000 and PEG 5000 are to be preferably used.

For cosmetic constituents, a different nomenclature is used; there, PEG is followed by a hyphen, which in turn is directly followed by a number which corresponds to the number n in the above-mentioned formula III. Using this nomenclature (so-called INCI nomenclature, CTFA International Cosmetic Ingredient Dictionary and Handbook, 5th edition, The Cosmetic, Toiletry and Fragrance Association, Washington 1997), e.g., PEG-32, PEG-40, PEG-55, PEG-60, PEG-75, PEG-100, PEG-150 and PEG-180 are to be preferably used according to the present invention.

Polyethylene glycols are commercially available, for example, under the trade names Carbowax® PEG 540 (Union Carbide), Emkapol® 6000 (ICI Americas), Lipoxol® 3000 MED (HÜLS America), Polyglycol® E-3350 (Dow Chemical), Lutrol® E4000 (BASF) and other trade names with higher numbers.

Polypropylene glycols (abbreviated as PPG) are polymers of propylene glycol which meet general formula IV



in which n can assume values between 1 (propylene glycol) and approximately 1000. Similarly as with the previously described PEGs, the salient factor in an evaluation of whether or not a

polypropylene glycol can be used in the context of the present invention is the aggregate state of the PPG, i.e., the melting point of the PPG must be higher than 30°C; as a result, the monomer (propylene glycol) and the lower oligomers with $n = 2$ to approximately 15 cannot be used, since they have a melting point lower than 30°C.

In addition to the PEGs and PPGs which are to be preferably used as dissolution-accelerating coating materials, other substances may, of course, also be used as long as they have a sufficiently high water solubility and a melting point higher than 30°C.

The molded cakes of washing or cleaning aids can contain varying quantities of coating material, auxiliary agents and active substance that is to be coated. In preferred embodiments, the coating material makes up 20 to 95 wt%, preferably 30 to 70 wt%, and especially 40 to 50 wt% of the molded cake.

At the processing temperature, which normally is higher than the softening temperature of the coating material, the active substances that are to be incorporated into the molded cakes of washing or cleaning aids can be used both in solid and in liquid forms as long as the molded cakes are available in solid form.

The active substances contained fulfill different tasks. By separating certain substances or by releasing additional substances in an accelerated or delayed manner, it is possible to improve the washing or cleaning performance. Active substances that are preferably incorporated into the molded cakes of the washing or cleaning aids are therefore those constituents of washing or cleaning agents which play a decisive role in the washing or cleaning process.

In preferred embodiments, the active substance or the active substances are therefore selected from the group of enzymes, bleaching agents, bleach activators, surfactants, corrosion inhibitors, deposition inhibitors, co-builders and/or odorous substances.

By incorporating surfactants into melted coating material, it is possible to produce a melt suspension and/or emulsion which, at a predetermined point in time, makes available additional substances with washing action in the finished molded cake of the washing or cleaning agent. For example, in this manner, it is possible to produce molded cakes for automatic dishwashers which release the additional surfactant only at temperatures reached by household dishwashers in the clear rinsing cycle. In this manner, additional surfactant is available in the clear rinsing cycle, which surfactant causes the water to run off more rapidly and thus effectively prevents spots on the dishes. Thus, today, if a suitable quantity of solidified melt suspension and/or emulsion is contained in the molded cakes, it is no longer necessary to use additional conventional clear rinse aids. Instead of separately dosing and measuring two products, only one molded cake can now be easily added; this saves time, effort and costs. Preferred active substance(s) in the molded cakes of washing or cleaning aids is/are therefore selected from the group of nonionic surfactants, in particular alkoxylated alcohols. These substances were described in detail above.

Another class of active substances which can be used to special advantage are bleaching agents. In this context, it is possible to produce molded cakes of washing or cleaning aids which release the bleaching agent only once a certain temperature is reached. Thus, there is a possibility of producing washing agents which enzymatically clean in the prerinsing cycle and which release the bleaching agent only in the main rinsing cycle. Similarly, it is possible to produce automatic dishwasher detergents which release the additional bleaching agent in the clear rinsing cycle and thus are able to more effectively remove tough stains, for example, tea stains.

In preferred embodiments, the active substance or active substances of the melt suspension or emulsion used in step (b) are therefore selected from the group of oxygen or halogen bleaching agents, in particular a chlorine bleaching agent. These substances have also already been discussed in detail.

Another class of compounds that can be preferably used as active substances in the molded cakes of washing or cleaning aids are the bleach activators. Known bleach activators are compounds comprising one or more N- or O-acyl groups, such as substances from the class of anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetyl ethylenediamine TAED, tetraacetyl methylenediamine TAMd and tetracetyl hexylenediamine TAHD, but also pentaacetyl glucose PAG, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine DADHT and isatoic acid anhydride ISA.

Bleach activators to be used are compounds which, when exposed to perhydrolysis conditions, generate aliphatic peroxocarboxylic acids with preferably 1 to 10 C atoms, in particular with 2 to 4 C atoms, and/or optionally substituted perbenzoic acid. Suitable substances are those which carry O- and/or N-acyl groups with the number of C atoms mentioned and/or optionally substituted benzoyl groups. Preferred are polyacylated alkylenediamines, in particular tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetyl glycouril (TAGU), N-acylimides, in particular N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, in particular n-nonanoyl or isononanoyl oxybenzenesulfonate (n- and iso-NOBS, respectively), carboxylic acid anhydrides, in particular phthalic acid anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran, n-methyl morpholinium acetonitrile methyl sulfate (MMA) and the enol esters known from DE 196 16 693 and DE 196 16 767, and acetylated sorbitol and mannitol and mixtures thereof (SORMAN), acylated sugar derivatives, in particular pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example, N-benzoyl caprolactam. Hydrophilic substituted acyl acetals and acyl lactams are also preferably used. Combinations of conventional bleach activators can be used as well.

In addition to or instead of the conventional bleach activators, it is also possible to incorporate so-called bleach catalysts into the molded cakes. These substances are bleach-enhancing transition metal salts and transition metal complexes, such as Mn, Fe, Co, Ru or Mo salen complexes or carbonyl complexes. In addition, Mn, Fe, Co, Ru, Mo, Ti V and Cu complexes with N-containing tripod ligands and Co, Fe, Cu and Ru ammine complexes are also usable bleach catalysts.

Preferably, bleach catalysts from the group of polyacylated alkylene diamines, in particular tetraacetyl ethylenediamine (TAED), in particular N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, in particular n-nonanoyl or iso-nonanoyl oxybenzenesulfonate (n- and iso-NOBS, respectively), n-methyl morpholinium acetonitrile methyl sulfate (MMA), preferably in quantities up to 10 wt%, in particular 0.1 wt% to 8 wt%, especially 2 to 8 wt%, and most preferably 2 to 6 wt%, relative to the overall agent.

Bleach-enhancing transition metal complexes, in particular with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of the manganese and/or cobalt salts and/or complexes, most preferably of the cobalt (ammine) complexes, the cobalt (acetate) complexes, the cobalt (carbonyl) complexes, the chlorides of cobalt or manganese, and manganese sulfate are used in conventional quantities, preferably in a quantity up to 5 wt%, in particular 0.0025 wt% to 1 wt%, and especially 0.01 wt% to 0.25 wt%, relative to the overall agent. In special cases, it is, however, also possible to use a greater quantity of bleach activator.

In addition, odorous substances can be incorporated as active substances. It is possible to use all odorous substances described in detail above as active substances. When odorous substances are incorporated into the molded cakes of washing or cleaning aids, one obtains washing or cleaning agents which release all or part of the perfume in a time-delayed manner. In this manner, the method according to the present invention allows the production, for example, of molded cakes for automatic dishwashers which allow the consumer to experience the perfume impression even after the dishwashing cycle is completed and when the door of the machine is opened. In this manner, the undesirable "alkali smell" which adheres to many automatic dishwashers can be eliminated.

In addition, corrosion inhibitors can also be incorporated as active substances, with the person skilled in the art being able to use the substances familiar to him. An effective deposition inhibitor was found to be, for example, a combination of an enzyme (e.g., lipase) and a lime soap dispersant.

Regardless of the class of materials used as active substances, the active substances or the active substances normally make up 5 to 50 wt%, preferably 10 to 45 wt%, and especially 20 to 40 wt% of the molded cakes of the washing or cleaning aids.

Such agents can be produced using any suitable method. Individually-portioned packages of washing or cleaning agents that are to be preferred, however, can be produced using a special method which will be described below.

Accordingly, another subject matter of the present invention relates to a method for the production of an individually-portioned package of cleaning agents which is characterized in that

- a) a molded cake of a washing or cleaning agent is produced,
- a) a molded cake of a washing or cleaning aid is produced,
- c) a suitable number of the molded cakes produced under a) and/or b) is filled into the individually-portioned package which is open at least on one side, and
- d) the individually-portioned package is sealed by applying a coat of a water-soluble material or a material that melts at a predetermined temperature on at least one portion of an inside wall of the open side of the package and by potentially compressing the open side of the package so as to form a sealing seam.

Process step a)

The molded cake of washing or cleaning agents produced in step a) can contain any components, in particular, however, the components already described above which are already contained in a particulate premix that is compressed to form molded cakes. Preferably these premixes have compositions which correspond to the compositions of the resultant molded cakes already described above. Regardless of the composition of the premixes to be compressed in process step a), the physical parameters of the premixes can be selected to ensure that advantageous molded cake properties result.

Thus, in the preferred variants of the method according to the present invention, the particulate premixes that are compressed in step a) have bulk densities higher than 600 g/L, preferably higher than 700 g/L, and especially higher than 800 g/L.

To obtain advantageous molded cake properties, the particle size in the premixes to be compressed can be adjusted as well. In preferred methods, the particulate premix that is compressed in step a) has a particle size distribution in which less than 10 wt%, preferably less than 7.5 wt%, and especially less than 5 wt%, of the particles are larger than 1600 μm or smaller than 200 μm . Relatively narrow particle size distributions are also to be preferred. Especially advantageous process variants are characterized in that the particulate premix compressed in step a) has a particle size distribution in which more than 30 wt%, preferably more than 40 wt% and especially more than 50 wt%, of the particles have a particle size between 600 and 1000 μm .

Process step a) of the method according to the present invention does not only provide for the compression of one particulate premix to form a molded cake with a well in the center of the surface. Instead, process step a) can also be extended so that multilayer molded cakes are

produced in a substantially known manner by preparing two or more premixes which are compressed one on top of the other. Thus, the premix first poured in is subjected to a mild preliminary compressive force so as to obtain a smooth upper surface that runs parallel to the bottom of the molded cake, and after the second premix has been added, the cake is compressed to form the finished molded cake. If the molded cakes have three or more layers, an additional preliminary compression takes place after each addition of the premix in question until the last premix has been added, at which time the cake is finally compressed to form the finished molded cake.

Because of the increasing complexity, in practice two-layer molded cakes are to be preferred. Thus, the above-described advantages can be obtained as early as in the intermediate step when certain components already described above are apportioned for inclusion in the separate layers.

Regardless of whether the molded cake has one or more phases, the premix is compacted in a so-called die between two punches to form a solid compressed cake. This procedure which hereinafter will be referred to as tableting is divided into four parts: dosing, compacting (elastic deformation), plastic deformation and ejection.

First, the premix is poured into the die, with the molding charge and thus the weight and the shape of the resultant molded cake being determined by the position of the lower punch and the shape of the compression mold. Consistent dosing, even when the throughput of molded cakes is high, is preferably ensured by means of volumetrically dosing the premix. As the tableting process continues, the upper punch touches the premix and moves downward into the direction of the lower punch. During this compaction, the particles of the premix are more tightly pressed against each other, while the volume of the cavities within the molding charge between the punches continually decreases. Beginning at a specific position of the upper punch (and thus beginning at a specific pressure exerted on the premix), plastic deformation sets in, in the course of which the particles coalesce and the molded cake is formed. Depending on the physical properties of the premix, a portion of the premix particles is crushed, and if the pressure increases even more, a sintering of the premix takes place. As the rate of compression increases, i.e., at high throughput quantities, the phase of elastic deformation is increasingly shortened so that the resultant molded cakes may have smaller or larger hollow spaces. In the last tableting step, the finished molded cake is ejected from the die by means of the lower punch and transported off by means of downstream transporting devices. At this time, only the weight of the molded cake is final since the shape and size of the molded pieces may change because of physical processes (elongation reversal, crystallographic effects, cooling, etc.). Tableting is carried out in commercially available tableting presses which can be fitted with single or double punches. In the latter case, not only the upper punch is used to build up pressure; instead, during

the compression process, the lower punch moves in the direction of the upper punch while the upper punch pushes down. For relatively small production quantities, eccentric tableting presses are preferably used, in which the punch or the punches are attached to an eccentric disk which, in turn, is mounted on a shaft around which it rotates at a predetermined speed of rotation. The movement of this punch can be compared to the mode of operation of a conventional four-stroke engine. The compression can be carried out with one upper and one lower punch; however, it is also possible for a plurality of punches to be mounted on an eccentric disk, in which case the number of die holes is correspondingly larger. Depending on the type used, the throughputs of eccentric presses vary from several hundred to a maximum of 3000 tablets per hour.

For larger throughputs, rotary tableting machines are used, in which a relatively large number of dies are arranged in a circle on a so-called die table. Depending on the model used, the number of dies varies between 6 and 55, with even larger dies being commercially available. On the die table, each die has an associated upper and lower punch; again, the compressive force can be actively built up either only by the upper or the lower punch or by both punches. The die table and the punches move around a common perpendicular shaft; while rotating, the punch is moved into the positions for filling, compaction, plastic deformation and ejection by means of curved rail-like tracks. In the areas in which an especially marked lifting or lowering of the dies is necessary (filling, compaction, ejection), these curved tracks are reinforced by additional push-down elements, pull-down rails and lifting tracks. The die is filled by means of a rigidly disposed feeding device, the so-called filling shoe, which is connected to a container in which the premix is stored. The molding pressure to be exerted on the premix can be individually adjusted by means of the pressure guideways for the upper and low punch, with the pressure being built up as the shaft heads of the dies roll past on adjustable pressure rollers.

To increase the throughput, rotary tableting machines can also be fitted with two filling shoes, in which case only half a circle has to be traveled through in order to produce one tablet. To produce two- or multilayered molded cakes, a plurality of filling shoes are arranged one behind the other, without the slightly molded first layer being ejected prior to the next filling. By means of a suitable process sequence, it is thus possible to produce press-coated tablets and bull's-eye tablets [unconfirmed translation], which have a structure reminiscent of onion skin, with the upper surface of the core or core layers of the bull's-eye tablets not being covered but instead remaining visible. Rotary tableting machines can also be equipped with single or multiple tools, thus making it possible, for example, for an outside circle with 50 and an inside circle with 35 holes to be used for simultaneously molding [the tablets]. The throughputs of modern rotary tableting machines are more than one million molded cakes per hour.

In the context of the present invention, tableting machines suitable for carrying out process step a) are commercially available from the firms of Apparatebau Holzwarth GbR,

Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen GmbH, Berlin, Mapag Maschinenbau AG, Bern (Switzerland), and Courtoy N. V., Halle (Belgium/Luxembourg). Especially suitable, for example, is the hydraulic double pressure press HPF 630 of LAEIS, Germany.

As already described, the molded cakes can be manufactured in predetermined shapes and predetermined sizes. An important feature of a method that is preferred according to the present invention is that the molded cakes which are produced in step a) have a well which, as will be described later in step b2), will be filled with the hot-melt suspension or emulsion produced in step b1). This well can have any desirable geometric shape, with the geometry of the well being independent of the geometry of the molded cakes. Thus, it is possible for round molded cakes to have round, elliptical, trigonal, tetragonal, pentagonal or polygonal wells. The shapes of the wells mentioned can also be implemented in rectangular or square molded cakes, and the corners of the molded cakes can be rounded. Even the side walls of the well can differ -- thus, all transitions from vertical side walls to flatter straight lines or curved well walls are possible. Especially suitable well geometries have been described in DE-A-198 22 973. The geometric factors disclosed in this document preferably also apply to the molded cakes with wells which are produced in step a) of the method according to the present invention.

After compression, the molded cakes of washing or cleaning agents have a high stability. The fracture strength of cylindrical molded cakes can be determined via the measured quantity of the diametral fracture stress. This fracture stress can be determined according to

$$\sigma = \frac{2P}{\pi Dt}$$

In this equation, σ stands for the diametral fracture stress (DFS) in Pa; P is the force in N which leads to the pressure which is exerted on the molded cake and which causes the fracture in the molded cake; D is the diameter of the molded cake in meters, and t is the height of the molded cakes.

Process step b)

In process step b), a molded cake of an auxiliary washing or cleaning agent is manufactured. This step can be carried out in the same manner as step a), except that the premix contains the components described for such auxiliary washing or cleaning agents.

In a preferred embodiment, the molded cake in step b) is produced by means of b1) production of a hot-melt suspension or emulsion from a coating material which has a melting point higher than 30°C and one or more active substances dispersed or suspended in said coating

material, b2) pouring the hot-melt suspension or emulsion at temperatures above the melting point of the coating material into suitable molds, and b3) subsequent cooling and, optionally, an after-treatment. Suitable coating materials that can be used in step b1) have already been described above.

At extremely low temperatures, for example, temperatures below 0°C, the coating material can be ruptured when it is exposed to impact or friction. To improve the stability at such low temperatures, additives may optionally be incorporated into the coating material. Suitable additives must be totally miscible with the melted wax, must not significantly change the melting range of the coating materials, must improve the elasticity of the coating material at low temperatures, must not increase the permeability of the coating material for water or humidity in general, and must not increase the viscosity of the melt of the coating material to the extent that processing is made more difficult or even impossible. Suitable additives which reduce the brittleness of a coating material -- which consists predominantly of paraffin -- at low temperatures are, for example, EVA copolymers, hydrogenated rosin acid methyl esters, polyethylene or copolymers of ethyl acrylate and 2-ethyl hexyl acrylate.

Another useful additive in cases in which paraffin is used as the coating material is a surfactant which should be added in a small quantity, for example, a C₁₂-C₁₈ fatty alcohol sulfate. This addition leads to an improved wetting of the material to be embedded by the coating material. The additive is preferably added in a quantity of approximately <5 wt%, preferably approximately <2 wt%, relative to the coating material. In many cases, using the additive can lead to the coating of active substances as well; without the additive, these active substances as a rule would form a tough plastic cake of paraffin and partially dissolved active substance after the coating material has melted.

In process step b) according to the present invention, it may be useful to add additional additives to the coating material so as to prevent, for example, a premature deposition of the active substances that are to be covered during cooling. The anti-deposition agents to be used which are also known as anti-settling agents are known from prior art, for example, from the production of paints and printing inks. To avoid sedimentation phenomena and concentration gradients of the substances to be coated during the transition from the plastic solidification region to the solid, for example, surface-active substances, waxes dispersed in solvents, montmorillonites, organically modified bentonites, (hydrogenated) castor oil derivatives, soybean lecithins, ethyl cellulose, low-molecular polyamides, metal stearates, calcium soaps or hydrophobed silicic acids can be used. Other substances that lead to the effects mentioned are selected from the groups of anti-flotation agents and thixotroping agents and are, chemically speaking, silicone oils (dimethyl polysiloxanes, methyl phenyl polysiloxanes, polyether-modified methyl alkyl polysiloxanes), oligomeric titanates and silanes, polyamines, salts of long-chain

polyamines and polycarboxylic acids, amine/amide-functional polyesters and amine/amide-functional polyacrylates.

The spectrum of commercially available additives of the classes of substances mentioned is very large. Commercial products which, in the context of the present invention, can be advantageously incorporated as additives are, for example, Aerosil® 200 (pyrogenic silicic acid, Degussa), Bentone SD-1, SD-2, 34, 52 and 57 (bentonite, Rheox), Bentone® SD-3, 27 and 38 (hectorite, Rheox), Tixogel® EZ 100 or VP-A (organically modified smectite, Südchemie), Tixogel® VG, VP and VZ (montmorillonite loaded with QAV, Südchemie), Disperbyk® 161 (block copolymer, Byk-Chemie), Borchigen® ND (ion exchanger free from sulfo groups, Borchers), Ser-Ad® FA 601 (Servo), Solsperse® (aromatic ethoxylate, ICI), Surfynol® types (Air Products), Tamol® and Triton® types (Rohm & Haas), Texaphor® 963, 3241 and 3250 (polymers, Henkel), Rilanit® types (Henkel), Thixcin® E and R (castor oil derivatives, Rheox), Thixatrol® ST and GST (castor oil derivatives, Rheox), Thixatrol® SR, SR 100, TSR and TSR 100 (polyamide polymers, Rheox), Thixatrol® 289 (polyester polymer, Rheox) and various M-P-A® types X, 60-X, 1078-X, 2000-X and 60-MS (organic compounds, Rheox).

Depending on the coating material and the material to be covered, the auxiliary agents mentioned can be used in varying quantities in the method according to the present invention. The conventional concentrations used for the anti-deposition, anti-flotation, thioxotrope and dispersing agents mentioned above are in a range from 0.5 to 8.0 wt%, preferably between 1.0 and 5.0 wt%, and especially between 1.5 and 3.0 wt%, relative to the hot-melt suspension or emulsion.

Thus, in the context of the present invention, it is preferable to use methods in which the hot-melt suspension or emulsion produced in step b) contains additional additives from the group of anti-deposition agents, anti-settling agents, anti-flotation agents, thioxotrope agents and dispersing aids in quantities of 0.5 to 8.0 wt%, preferably between 1.0 and 5.0 wt%, and especially between 1.5 and 3.0 wt%, relative to the hot-melt suspension or emulsion.

The use of special emulsifying agents is useful especially in the production of hot-melt suspensions and/or emulsions which contain active substances that are liquid at the processing temperature. It was found that especially emulsifying agents from the group of fatty alcohols, fatty acids, polyglycerol esters and polyoxyalkylene siloxanes are extremely well suited for this purpose.

In this context, fatty alcohols are defined as alcohols with 6 to 22 carbon atoms which can be obtained from the native fats and/or oil via the corresponding fatty acids (see below). Depending on the origin of the fat and/or oils from which they are obtained, these alcohols can be substituted in the alkyl chain and unsaturated in certain regions.

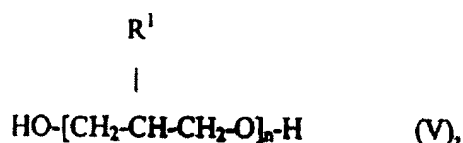
Thus, in process step b), the emulsifying agents preferably used are C₆-C₂₂ fatty alcohols, preferably C₈-C₂₂ fatty alcohols, and especially C₁₂-C₁₈ fatty alcohols, with special preference being given to the C₁₆-C₁₈ fatty alcohols.

Furthermore, all fatty acids obtained from vegetable or animal oils and fats can be used as emulsifying agents. Regardless of their aggregate state, the fatty acids may be saturated or mono- to polysaturated. The species of unsaturated fatty acids which are solid at room temperature are to be preferred over the liquid and pasty species. Naturally, not only "pure" fatty acids, but also the technical fatty acid mixtures obtained during the cleavage from fats and oils can be used; from the economical standpoint, these mixtures are definitely to be preferred.

In the context of the present invention, it is thus possible to use, for example, separate species or mixtures of the following acids as emulsifying agents: caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-octadecanoic acid, arachinic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid, 10-undecenic acid, petroselic acid, petroselaidic acid, oleic acid, elaidic acid, ricinolic acid, linolaidic acid, α - and β -eleostearic acid, gadoleic acid, erucic acid, and brassidic acid. Naturally, the fatty acids with an uneven number of C atoms can also be used, for example, undecanoic acid, tridecanoic acid, pentadecanoic acid, heptadecanoic acid, nonadecanoic acid, heneicosanic acid, tricosanic acid, pentacosanic acid, and heptacosanic acid.

In preferred process steps b), C₆-C₂₂ fatty acids, preferably C₈-C₂₂ fatty acids, and especially C₁₂-C₁₈ fatty acids, can be used, with special preference being given to the C₁₆ to C₁₈ fatty acids.

In the context of the present invention, polyglycerol esters, in particular esters of fatty acids with polyglycerols, are emulsifying agents that are to be especially preferred. The preferred polyglycerol esters can be described by general formula V



in which R¹ in each glycerol unit, independently of each other, stands for H or for a fatty acyl residue with 8 to 22 carbon atoms, preferably with 12 to 18 carbon atoms, and n stands for a number between 2 and 15, preferably between 3 and 10.

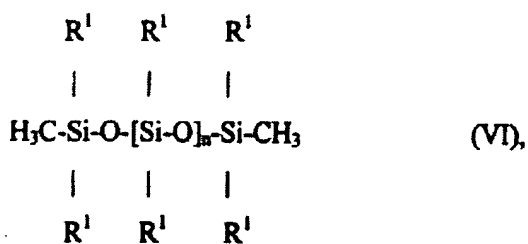
These polyglycerol esters are known and commercially available, especially those with degrees of polymerization of n = 2, 3, 4, 6 and 10. Since substances of the type mentioned are also widely used in cosmetic formulations, a number of these substances are also classified in the

INCI nomenclature (CFTA International Cosmetic Dictionary and Handbook, 5th edition, The Cosmetic, Toiletry and Fragrance Association, Washington, 1997). This standard work on cosmetics contains, for example, information about keywords, such as

POLYGLYCERYL-3-BEESWAX, POLYGLYCERYL-3-CETYL ETHER, POLYGLYCERYL-4-COCOATE, POLYGLYCERYL-10-DECALINOLEATE, POLYGLYCERYL-10-DECAOLEATE, POLYGLYCERYL-10-DECASTEARATE, POLYGLYCERYL-2-DIISOSTEARATE, POLYGLYCERYL-3-DIISOSTEARATE, POLYGLYCERYL-10-DIISOSTEARATE, POLYGLYCERYL-2-DIOLEATE, POLYGLYCERYL-3-DIOLEATE, POLYGLYCERYL-6-DIOLEATE, POLYGLYCERYL-10-DIOLEATE, POLYGLYCERYL-3-DISTEARATE, POLYGLYCERYL-6-DISTEARATE, POLYGLYCERYL-10-DISTEARATE, POLYGLYCERYL-10-HEPTAOLEATE, POLYGLYCERYL-12-HYDROXYSTEARATE, POLYGLYCERYL-10-HEPTASTEARATE, POLYGLYCERYL-6-HEXAOLEATE, POLYGLYCERYL-2-ISOSTEARATE, POLYGLYCERYL-4-ISOSTEARATE, POLYGLYCERYL-6-ISOSTEARATE, POLYGLYCERYL-10-LAURATE, POLYGLYCERYLMETHACRYLATE, POLYGLYCERYL-10-MYRISTATE, POLYGLYCERYL-2-OLEATE, POLYGLYCERYL-3-OLEATE, POLYGLYCERYL-4-OLEATE, POLYGLYCERYL-6-OLEATE, POLYGLYCERYL-8-OLEATE, POLYGLYCERYL-10-OLEATE, POLYGLYCERYL-6-PENTAOLEATE, POLYGLYCERYL-10-PENTAOLEATE, POLYGLYCERYL-6-PENTASTEARATE, POLYGLYCERYL-10-PENTASTEARATE, POLYGLYCERYL-2-SESQUIISOSTEARATE, POLYGLYCERYL-2-SESQUIOLEATE, POLYGLYCERYL-2-STEARATE, POLYGLYCERYL-3-STEARATE, POLYGLYCERYL-4-STEARATE, POLYGLYCERYL-8-STEARATE, POLYGLYCERYL-10-STEARATE, POLYGLYCERYL-2-TETRAISOSTEARATE, POLYGLYCERYL-10-TETRAOLEATE, POLYGLYCERYL-2-TETRASTEARATE, POLYGLYCERYL-2-TRIISOSTEARATE, POLYGLYCERYL-10-TRIOLEATE, POLYGLYCERYL-6-TRISTEARATE.

The commercially available products made by different manufacturers which are classified in the handbook mentioned under the keywords listed above can be advantageously used as emulsifying agents in process step b) according to the present invention.

Another group of emulsifying agents which can be used in process step b) according to the present invention includes substituted silicones with side chains that were reacted with ethylene and propylene oxide. Such polyoxyalkylene siloxanes can be described by the following general formula VI



in which each residue R^1 , independently of each other, stands for $-\text{CH}_3$ or a polyoxyethylene or polyoxypropylene group $-\text{CH}(\text{R}^2)-\text{CH}_2-\text{O}]_x\text{H}$ group; R^2 stands for H or $-\text{CH}_3$; x stands for a number between 1 and 100, preferably between 2 and 20, and especially a number lower than 10, and n denotes the degree of polymerization of the silicone.

The polyoxyalkylene siloxanes can optionally also be etherified or esterified in the free OH groups of the polyoxyethylene and polyoxypropylene side chains. In the INCI nomenclature,

the unetherified and unesterified polymer of dimethyl siloxane with polyoxyethylene and/or polyoxypropylene is called DIMETHICONE COPOLYOL and is commercially available under the trade name of Abil® B (Goldschmidt), Alkasil® (Rhône-Poulenc), Silwet® (Union Carbide) or Belsil® DMC 6031.

The DIMETHICONE COPOLYOL ACETATE esterified with acetic acid (for example, Belsil® DMC 6032, -33 and -35, Wacker) and the DIMETHICONE COPOLYOL BUTYL ETHER (e.g., KF352A, Shin Etsu) can also be used as emulsifying agents within the context of process step b1) according to the present invention.

Like the coating materials and the substances to be coated, the emulsifying agents can be used in a widely varying range. Generally, the emulsifying agents of the type mentioned make up 1 to 25 wt%, preferably 2 to 20 wt% and especially 5 to 10 wt%, of the weight of the hot-melt suspension and/or emulsion.

In the preferred methods, the hot-melt suspension or emulsion that was produced in step b1) also comprises emulsifying agents from the group of fatty alcohols, fatty acids, polyglycerol esters and/or polyoxyalkylene siloxanes in quantities of 1 to 20 wt%, preferably 2 to 15 wt%, and especially 2.5 to 10 wt%, relative to the hot-melt suspension or emulsion.

Process steps b2 and b3)

In process step b2), the hot-melt suspension or emulsion is poured into suitable molds. These molds can have any shape, and this shape determines the shape of the molded cakes of auxiliary washing or cleaning agents obtained. It is to be especially preferred, however, if the molds are the molded cakes with wells which were manufactured in step a) and which are filled with the separately manufactured hot-melt suspension or emulsion at temperatures higher than the melt temperature of the coating material. The temperature of the melt to be poured in can be randomly high; however, with respect to temperature-sensitive components, it is preferable to ensure that process step b2) is carried out at temperatures which are at most 10°C, preferably at most 5°C and especially at most 2°C, above the solidification temperature of the hot-melt suspension or emulsion.

The hot-melt suspension or emulsion is preferably metered into the well of the previously produced molded cakes by means of a piston-type dosing machine, a pneumatic pump, a peristaltic pump or a gear-type pump.

These pumps are known to the person skilled in the art; thus, depending on the composition of the hot-melt suspension or emulsion, he will have no problem selecting the proper pump with respect to dimension, material and mode of operation. For hot-melt suspensions or emulsions that contain surfactants, bleaching agents or odorous substances, it was found that the piston-type pumps are especially suitable.

Prior to pouring the melt into the molded cakes, said cakes can be pretreated so as to ensure that the adhesion of the melt to the well is improved. Thus, it is, for example, possible to apply a suitable coupling agent to the surface of the wells, which coupling agent ensures adhesion of the melt to the molded cake so that the solidified material that fills the well cannot separate from the molded cake during shipping and handling.

A more elegant and simpler technical solution provides for heating the molded cakes with wells prior to filling them with the hot-melt suspension or emulsion and thereby to improve adhesion of the solidifying melt. In this manner, the solidifying melt can at least partly penetrate the marginal areas of the well and, on solidification, ensure a permanent and stable adhesive bond.

In another preferred embodiment, it is, in fact, desirable for the molded cakes to easily separate once the melt has solidified. Again, it may be useful to pretreat the molded cakes prior to filling them with the melt in order to improve the separation of the melt from the well. Thus, it is, for example, possible to apply suitable release agents to the surfaces of the wells, which release agents reduce the adhesion of the melt to the molded cake. It may suffice, however, if the molded cakes with wells are cooled prior to filling them with the hot-melt suspension or emulsion so as to reduce the adhesion of the solidifying melt.

The melt can be solidified either at room temperature, or the solidification may be accelerated by cooling the melt. After solidification of the melt, the molded cakes are preferably mechanically removed from the well or mold and can optionally be fed to additional shaping steps, such as the removal of flash.

Process step c)

In process step c), a suitable number of molded cakes produced in steps a) and b) are fed into an appropriately shaped package that is open at least on one side. A suitable number is here defined to mean a number of molded cakes of washing or cleaning agents or molded cakes of auxiliary washing or cleaning agents as would be advantageously required in one single portion for one washing or cleaning cycle. It is of special advantage if the quantities of the washing or cleaning agent and of the auxiliary washing or cleaning agents are adjusted with respect to each other by the number in which they are contained in each dose. As already described earlier, the appropriately shaped packages are preferably individually-portioned pouches which can be made of a water-soluble or water-insoluble material.

Process step d)

In step d), the filled individually-portioned package is subsequently sealed by applying a water-soluble material or a material that melts at a predetermined temperature to at least one

portion of the inside wall of the open side of the package and, optionally, by applying pressure to the open side of the package so as to form a sealing seam.

The water-soluble or meltable materials are the materials that have already been described above. In this context, it may be useful, on the one hand, if the materials or parts thereof are components of washing or cleaning agents, and it is preferable, on the other hand, to use water-soluble adhesives or hot-melt adhesives, such as have already been described above.

It is useful to subsequently seal the package by applying pressure to the coated wall or walls. The resultant sealing seam seals the package during storage and shipping, and the components are released either by dissolution of the sealing seam in water or, if a meltable material has been used, by melting the material when the temperature increases.

In another embodiment, the package can be closed by crimping. If this approach is used, the edges of the folded package are folded over several times and are subsequently pressure-embossed. Such a closure has the advantage that it is more difficult for humidity to access the sealing seam, which increases the stability of the package during storage.

Examples

Production of detergent tablets for use in automatic dishwashers

Process step a)

Production of molded cakes with wells

By compacting two different premixes, rectangular two-layer molded cakes with a well in the shape of a semiellipse were manufactured. The molded cakes were comprised of 75 wt% of a lower phase and 25 wt% of an upper phase. The composition (in wt% relative to the premix used) of the two premixes and thus of the two different phases of the molded cakes with wells is shown in the table below:

	① Vorgemisch 1 (Unterphase)	② Vorgemisch 2 (Oberphase)
③ { Natriumcarbonat	32,0	-
Natriumtripolyphosphat	52,0	91,4
Natriumperborat	10,0	-
Tetraacetyl ethylendiamin	2,5	-
Benzotriazol	1,0	-
C ₁₂ -Fettalkohol mit 3 EO	2,5	-
Farbstoff		0,2
Enzyme		6,0
Parfüm		0,4
Silikonöl		2,0

Key: 1 Premix 1 (lower phase)
 2 Premix 2 (upper phase)
 3 Sodium carbonate
 Sodium tripolyphosphate
 Sodium perborate
 Tetraacetyl ethylenediamine
 Benzotriazole
 C₁₂ fatty alcohol with 3 EO
 Dye
 Enzymes
 Perfume
 Silicone oil

Process step b1)

Production of hot-melt suspensions/emulsions

By heating the coating material and by stirring in the active substances and optional auxiliary agents, three hot-melt dispersions/emulsions SDE 1 through 3 were prepared, the composition (wt% relative to the melt) of which is shown in the table below:

	① SDE 1 (Bleichkern)	② SDE 2 (Tensidkern)	③ SDE 3 (Duftkern)
④ Paraffin 57-60°C	50,0	60,0	95,0
Dichloroisocyanursäure	35,0	-	-
Poly Tergent SLF-18B-45*	-	33,3	-
Parfüm	-	-	5,0
Tylose MH 50	15,0	-	-
Polyglycerin-12-hydroxystearat	-	6,7	-

⑤ *: Alkoholalkoxylat der Firma Olin Chemicals, Erweichungspunkt 25-45°C

- Key:
- 1 SDE 1 (hot-melt dispersion/emulsion 1)
 - 2 SDE 2 (hot-melt dispersion/emulsion 2)
 - 3 SDE 3 (hot-melt dispersion/emulsion 3)
 - 4 Paraffin 57-60°C
Dichloroisocyanuric acid
Poly Tergent SLF-18B-45*
Perfume
Tylose MH 50
Polyglycerol-12-hydroxystearate
 - 5 * Alcohol alkoxylate of Olin Chemicals, softening point 25-45°C

Process step b2)

Pouring the hot-melt suspensions/emulsions into the molded cakes

The hot-melt dispersions/emulsions prepared in step b1) in the following weight ratios (given in wt% relative to the filled finished molded cake) were poured into the molded cakes that had been prepared in process step a); the molded cakes had been heated to 40°C prior to filling them:

	① Muldenformkörper mit Bleichmittelkern	② Muldenformkörper mit Tensidkern	③ Muldenformkörper mit Parfümkern
④ Muldenformkörper	96,0	96,0	96,0
SDE 1	4,0	-	-
SDE 2	-	4,0	-
SDE 3	-	-	4,0

- Key: 1 Molded cake with well with core of bleaching agent
 2 Molded cake with well with surfactant core
 3 Molded cake with well with perfume core
 4 Molded cake with well
 SDE 1 (hot-melt dispersion/emulsion 1)
 SDE 2 (hot-melt dispersion/emulsion 2)
 SDE 3 (hot-melt dispersion/emulsion 3)

Process step b3)

Cooling and after-treatment

The filled molded cakes were allowed to cool at room temperature, and subsequently, the hot-melt cores were mechanically removed from the center.

Process steps c) and d)

Packaging

One tablet with a well and one hot-melt core each are placed into a pouch which had previously be manufactured from polypropylene film and which was open on one side. The film is sealed using a water-soluble adhesive.

The examples above show molded cakes in which the hot-melt core is released by means of delayed dissolution. In other examples, hot-melt dispersions of n-methyl morpholinium acetonitrile methyl sulfate (MMA) in readily soluble coating materials were produced, which demonstrate the positive effects even when the release is accelerated. According to process step a) described above, molded cakes with wells were produced. By heating the coating material and stirring in the active substance (MMA), hot-melt dispersions SDE 4 through 8 were obtained, the composition (wt% relative to the melt) of which is listed in the table below:

	①	②	③	④	⑤
	SDE 4	SDE 5	SDE 6	SDE 7	SDE 8
⑥ Sokalan®-BM 1*	44,0	50,0	60,0	60,0	60,0
PEG 1550 (Smp. 45–50 °C)	44,0	50,0	40,0	-	-
PEG 3000 (Smp. 50–56 °C)	-	-	-	40,0	-
PEG 4000	-	-	-	-	40,0
Citronensäure	4,8	-	-	-	-
Natriumhydrogencarbonat	7,2	-	-	-	-

⑦ * n-Methyl-Morpholinium-Acetonitril-Methylsulfat (MMA), ca. 50% auf Träger (BASF)

- Key: 1 SDE 4 (hot-melt dispersion/emulsion 4)

- 2 SDE 5 (hot-melt dispersion/emulsion 5)
- 3 SDE 6 (hot-melt dispersion/emulsion 6)
- 4 SDE 7 (hot-melt dispersion/emulsion 7)
- 5 SDE 8 (hot-melt dispersion/emulsion 8)
- 6 Sokalan®-BM1*
PEG 1550 (melting point 45-50°C)
PEG 3000 (melting point 50-56°C)
PEG 4000
Citric acid
Sodium hydrogen carbonate
- 7 * n-Methyl morpholinium acetonitrile methyl sulfate (MMA), approximately 50%
on carrier (BASF)

Claims

1. An agent for machine washing or cleaning, in particular for use in an automatic dishwasher, characterized in that it comprises a component which is active during a first washing or cleaning cycle and a component which is active during a subsequent washing or cleaning cycle and that both components together are packed in an individually-portioned package, without the need of removing the components from the individual portion packages prior to using the agent.

2. The agent as claimed in Claim 1, characterized in that the individually-portioned package is a pouch made of a substantially water-insoluble material, which pouch is sealed with a water-soluble material.

3. The agent as claimed in Claim 1, characterized in that the individually-portioned package is a pouch made of a substantially water-insoluble material, which pouch has at least one sealing seam which releases the pouch contents at a predetermined temperature.

4. The agent as claimed in either of Claims 2 or 3, characterized in that the sealing seam contains an active washing or cleaning agent which is selected from the normally used constituents of washing or cleaning agents.

5. The agent as claimed in one of Claims 2 through 4, characterized in that the sealing seam is made of a meltable substance, in particular, a hot-melt adhesive.

6. The agent as claimed in any one of Claims 1 through 5, characterized in that the individually-portioned pouch has a mounting device disposed on it.

7. The agent as claimed in Claim 6, characterized in that the mounting device is a means which allows the detachable attachment of the individually-portioned package in an automatic washing and cleaning machine, in particular, an automatic dishwasher, so that the empty package can be removed after the washing or cleaning cycle has been completed.

8. The agent as claimed in either Claim 6 or 7, characterized in that the mounting device is a means which allows a detachable adhesion of the individually-portioned package to the wall of the automatic washing and cleaning machine, in particular, the automatic dishwasher.

9. The agent as claimed in either Claim 6 or 7, characterized in that the mounting device is a means which makes it possible to suspend the individually-portioned package in the automatic washing or cleaning machine, in particular, the automatic dishwasher.

10. The agent as claimed in either Claim 6 or 7, characterized in that the mounting device is a means which, in combination with a counterpiece which is permanently connected to the automatic washing and cleaning machine, in particular the automatic dishwasher, makes possible a detachable attachment of the individually-portioned package.

11. The agent as claimed in Claim 10, characterized in that the mounting device is a hook and loop fastener, with one part of the fastener being attached to the upper surface on the inside of the automatic washing or cleaning machine, in particular, of the automatic dishwasher.

12. The agent as claimed in any one of Claims 1 through 11, characterized in that the contents of the individually-portioned pouch are molded cakes, in particular, at least one compressed and one uncompressed molded cake.

13. The agent as claimed in any one of Claims 1 or 6 through 12, characterized in that the individually-portioned package is a pouch made of a water-soluble material.

14. The agent as claimed in any one of Claims 1 through 13, characterized in that the component that is active during a first washing or cleaning cycle is a component which is active during the main rinsing cycle of an automatic dishwasher and that the component which is active during a subsequent washing or cleaning cycle is a component which is active during the clear rinsing cycle of an automatic dishwasher.

15. The agent as claimed in any one of Claims 1 through 14, characterized in that the component which is active during a first washing or cleaning cycle is a washing or cleaning agent, in particular, a molded cake of a washing or cleaning agent, and that the component which is active during a subsequent washing or cleaning cycle is an auxiliary washing or cleaning agent, in particular, a molded cake of an auxiliary washing or cleaning agent.

16. The agent as claimed in Claim 15, characterized in that the washing or cleaning agent comprises builders in quantities of 20 to 80 wt%, preferably 25 to 75 wt%, and especially 30 to 70 wt%, as well as surfactant(s), preferably nonionic surfactant(s), in quantities of 0.5 to 10 wt%, preferably 0.75 to 7.5 wt%, and especially 1.0 to 5 wt%.

17. The agent as claimed in either Claim 15 or 16, characterized in that the washing or cleaning agent is available in the form of a multilayer molded cake, in particular, in the form of a two-layer molded cake, in which preferably several, in particular two different phases are present.

18. The agent as claimed in Claim 17, characterized in that one of the phases comprises one or more bleaching agents and the other phase comprises one or more enzymes.

19. The agent as claimed in Claim 17, characterized in that one of the phases comprises one or more bleaching agents and the other phase comprises one or several bleach activators.

20. The agent as claimed in any one of Claims 15 through 19, characterized in that the molded cake of an auxiliary washing or cleaning agent comprises a coating material with a melting range from 45°C to 75°C which preferably comprises at least one paraffin wax with a melting range from 50°C to 55°C.

21. The agent as claimed in Claim 20, characterized in that the coating material comprises at least one substance from the group of polyethylene glycols (PEG) and/or polypropylene glycols (PPG).

22. The agent as claimed in either Claim 20 or 21, characterized in that the coating material makes up 20 to 95 wt%, preferably 30 to 70 wt%, and especially 40 to 50 wt%, of the molded cake and that the active substance or active substances in the molded cake of the auxiliary washing or cleaning agent is/are selected from the group of enzymes, bleaching agents, preferably from the group of oxygen or halogen bleaching agents, in particular, chlorine bleaching agents, bleach activators, in particular, from the groups of polyacylated alkylene diamine, in particular, tetraacetyl ethylenediamine (TAED), of the N-acylimides, in particular, N-nonanoyl succinimide (NOSI), of the acylated phenol sulfonates, in particular, n-nonanoyl or isononanoyl oxybenzene sulfonate (n- and iso-NOBS, respectively), n-methyl morpholinium acetonitrile methyl sulfate (MMA), surfactants, preferably from the group of nonionic surfactants, in particular, of the alkoxyated alcohols, corrosion inhibitors, deposition inhibitors, co-builders and/or odorous substances.

23. A method for the production of an individually-portioned package containing a washing or cleaning agent, characterized in that

- a) a molded cake of a washing or cleaning agent is produced,
- a) a molded cake of an auxiliary washing or cleaning agent is produced,
- c) a suitable number of the molded cakes produced under a) and/or b) are filled into the individually-portioned package which is open at least on one side, and
- d) the individually-portioned package is sealed by applying a coat of a water-soluble material or a material that melts at a predetermined temperature to at least one portion of an inside wall of the open side of the package and by optionally applying pressure to the open side of the package so as to form a sealing seam.

24. The method for producing an individually-portioned package containing a washing or cleaning agent as claimed in Claim 23, characterized in that the molded cake in step b) is produced by means of b1) production of a hot-melt suspension or emulsion from a coating

material which has a melting point higher than 30°C and one or more active substances dispersed or suspended in said coating material, b2) pouring the hot-melt suspension or emulsion at temperatures above the melting point of the coating material into suitable molds, and b3) subsequent cooling and, optionally, an after-treatment.

25. The method as claimed in either Claims 23 or 24, characterized in that in step a) a particulate premix is compressed.

26. The method as claimed in Claim 25, characterized in that the premix preferably comprises builders in quantities of 20 to 80 wt%, preferably 25 to 75 wt% and especially 30 to 70 wt%, relative to the premix, as well as surfactant(s), preferably nonionic surfactant(s), in quantities of 0.5 to 10 wt%, preferably 0.75 to 7.5 wt%, and especially 1.0 to 5.0 wt%, relative to the premix.

27. The method as claimed in either Claim 25 or 26, characterized in that the particulate premix that had been compressed in step a) has a bulk density higher than 600 g/L, preferably higher than 700 g/L, and especially higher than 800 g/L.

28. The method as claimed in one of Claims 25 through 27, characterized in that the particulate premix that had been compressed in step a) has a particle size distribution in which less than 10 wt%, preferably less than 7.5 wt%, and especially less than 5 wt%, of the particles are larger than 1600 µm or smaller than 200 µm and that the premix most preferably has a particle size distribution in which more than 30 wt% , preferably more than 40 wt%, and especially more than 50 wt%, of the particles have a particle size between 600 and 1000 µm.

29. The method as claimed in any one of Claims 23 through 28, characterized in that in step a) multilayer molded cakes are produced in a substantially known manner by compressing several different particulate premixes one on top of the other.

30. The method as claimed in Claim 29, characterized in that in step a) two-layer molded cakes are produced by compressing two different particulate premixes one on top of the other, one of which premixes comprises one or more bleaching agents and the other comprises one or more enzymes.

31. The method as claimed in either Claim 29 or 30, characterized in that in step a) two-layer molded cakes are produced by compressing two different particulate premixes one on top of the other, one of which premixes comprises one or more bleaching agents and the other comprises one or more bleach activators.

32. The method as claimed in any one of Claims 23 through 31, characterized in that in step a) molded cakes which have a well are produced.

33. The method as claimed in any one of Claims 24 through 32, characterized in that the coating material in step b) has a melting range from 45°C to 75°C and preferably comprises a paraffin wax with a melting range of 50°C to 55°C.

34. The method as claimed in any one of Claims 24 through 33, characterized in that the coating material comprises at least one substance from the group of polyethylene glycols (PEG) and/or polypropylene glycols (PPG).

35. The method as claimed in any one of Claims 24 through 34, characterized in that the coating material makes up 20 to 95 wt%, preferably 30 to 70 wt%, and especially 40 to 50 wt%, of the hot-melt suspension or emulsion produced in step b1) and that the active substance(s) in the hot-melt suspension or emulsion produced in step b1) is/are selected from the group of enzymes, bleaching agents, preferably from the group of oxygen or halogen bleaching agents, in particular, chlorine bleaching agent, bleach activators, in particular, from the groups of polyacylated alkylenediamines, in particular, tetraacetyl ethylenediamine (TAED), of N-acylimides, in particular, N-nonanoyl succinimide (NOSI), of acylated phenol sulfonates, in particular, n-nonanoyl or isononanoyl oxybenzenesulfonate (n- and iso-NOBS, respectively), n-methyl morpholinium acetonitrile methyl sulfate (MMA), surfactants, preferably from the group of nonionic surfactants, in particular, of the alkoxyated alcohols, corrosion inhibitors, deposition inhibitors, co-builders and/or odorous substances.

36. The method as claimed in any one of Claims 24 through 35, characterized in that the active substance(s) make(s) up 5 to 50 wt%, preferably 10 to 45 wt% and in particular 20 to 40 wt%, of the hot-melt suspension or emulsion that was produced in step b1).

37. The method as claimed in any one of Claims 24 through 36, characterized in that the hot-melt suspension or emulsion produced in step b1) comprises additional auxiliary agents from the group of anti-deposition agents, anti-settling agents, anti-flotation agents, thixotroping agents and dispersing aids in quantities of 0.5 to 8.0 wt%, preferably between 1.0 and 5.0 wt%, and in particular, between 1.5 and 3.0 wt%, relative to the hot-melt suspension or emulsion.

38. The method as claimed in any one of Claims 24 through 37, characterized in that the hot-melt suspension or emulsion produced in step b1) additionally comprises emulsifying agents from the group of fatty alcohols, fatty acids, polyglycerol esters and/or polyoxyalkylene siloxanes in quantities of 1 to 20 wt%, preferably 2 to 15 wt%, and in particular, 2.5 to 10 wt%, relative to the hot-melt suspension or emulsion.

39. The method as claimed in any one of Claims 24 through 38, characterized in that process step b2) is carried out at temperatures which are at most 10°C, preferably at most 5°C, and in particular, at most 2°C, above the solidification temperature of the hot-melt suspension or emulsion and that the hot-melt suspension or emulsion is filled into the molds by means of a piston-type dosing pump, a pneumatic pump, a peristaltic pump or a gear-type pump.

40. The method as claimed in any one of Claims 24 through 39, characterized in that the suitable molds in step b2) are wells which hold the molded cakes from step a).